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# REFINING VEGETABLE AND ANIMAL OILS.*

BY

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THE terms "fat" and "wax" are commonly applied, more or less indiscriminately, to solid substances which have a greasy feeling to the touch and do not dissolve in water. Physically, waxes are regarded as having generally a harder consistency than fats. Chemically, fats are usually compounds of the trihydric alcohol, glycerol, $C_3H_5(OH)_3$; while the waxes are compounds of monohydric alcohols of large molecular weight; for example, cetyl alcohol, $C_{16}H_{33}OH$; myristic alcohol, $C_{30}H_{61}OH$, and cholesterol, $C_{27}H_{45}OH$. The names applied to some of these substances do not lessen the confusion; for example, "wool fat" and "spermaceti" are compounds of cholesterol and cetyl alcohol, hence are in reality waxes; while "Japan wax," a compound of glycerol, is actually a fat.

A fat, such as is indicated above, has among other physical properties a characteristic melting-point. Those which are liquid at ordinary temperatures are called *oils*. It is of such substances more especially that this communication deals with, although reference will be made to cocoanut oil, which may or may not be a solid at ordinary temperatures, therefore technically might be regarded as a fat.

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It will be understood that the term "oil," as here used, is not to be associated with the natural or petroleum oils, *i.e.*, hydrocarbon oils, or the essential oils, both classes of which in general exhibit in a way the physical but not the chemical properties, necessarily, referred to above.

Fats are widely distributed in the vegetable and animal kingdoms, and, referring to the former only for the time being, we may say they are primarily glycerides of oleic, palmitic, and stearic acids. These fats are found *mainly*, but not necessarily, in the reproductive bodies, such as spores and seeds. They are found in spores, sexual and asexual, of many algæ. In angiosperms they are widely distributed, replacing, wholly or in part, carbohydrates as reserve food material, and they are often associated with protein reserves; for example, in the seed from which colza oil, palm oil, cotton-seed oil, linseed oil, olive oil, and cocoa butter are obtained. It is present, perhaps, as a reserve food material, associated with starch, in some tubers. The starch in the parenchyma of the stem of certain plants may be converted into fat during the winter's cold, and *vice versa*, when there is a rise of temperature in the summer time. Without venturing into the misty etiology involved, we may, for our purposes, realize the likelihood of the presence of carbohydrates, proteins, and other substances derived therefrom, as gums, etc., in oils obtained from these sources by the various means to be referred to later.

These oil-containing bodies invariably contain some coloring matter. Some of the coloring matters appear to be essential for certain of the changes just referred to. The most prominent pigment appears to be chlorophyll, an ester of tricarboxylic acid, chlorophyllin, $C_{31}H_{39}N_4Mg(COOH)_3$, and is the normal green coloring matter of plants. It may easily be broken down into substances that contain magnesium and substances that do not contain that metal.

Accompanying the chlorophyll are several pigments more or less insoluble in the cell sap; namely, carotin ($C_{40}H_{56}$), yellow to red in color, and xanthophyll ($C_{40}H_{56}O_2$), a neutral body, yellow to orange in transmitted light. These substances may be destroyed by the action of such powerful chemical agents as concentrated sulphuric acid, especially if heated in the presence of oxygen.

Closely related to the fats is a group of substances known as phosphatides or lecithins. Occurring in egg-yolk to about 9 per

cent., we find them to the extent of from 0.25 to 1.75 per cent. in cereals and leguminous seeds, hence they appear in the oils extracted from the seed. They are glycerol esters, two of the acidities being neutralized by fatty acids, the third being saturated by a combination of phosphoric acid and choline, as shown here.

$$\begin{array}{l} CH_2O_2C.C_{17}H_{35} \\ | \\ CHO_2C.C_{17}H_{35} \\ | \\ CH_2 - OP.O.OH.O.C_5H_{13}N.OH \end{array}$$

It is easily broken up by lipase, and hydrolyzed by boiling with alkalies and acids.

We always also find a small quantity of unsaponifiable residue in fats, which is in the main composed of the monohydric alcohols, cholesterol, $C_{27}H_{45}OH$, and phytosterol, the latter now being a generic term for a group of allied substances, with formulas varying from $C_{27}H_{45}OH$ (sitosterol) to $C_{30}H_{47}OH$ (stigmosterol). Cholesterol occurs in the bile, brain, and blood of animals, and is the chief alcohol constituent of wool-fat. All vegetable fats contain phytosterol, the amount varying from 0.1 to 0.3 per cent., being even higher in the oil obtained from certain peas and beans, especially Calabar beans.

The oils are extracted by disintegration of the mass involving a disruption of the oil-sacs: (*a*) with a suitable solvent; (*b*) rendering by heat, with or without water; (*c*) or pressure, mechanical, applied when the mass is cold or hot.

If the mass extracted be selected and perfectly clean and fresh, the oil or fat obtained is usually neutral and "sweet." The exigencies of commercial operation do not admit of these conditions, however, so the oil or fat produced is usually acid and more or less contaminated. The contaminations may be quite normal and natural. They may be bacterial in nature and also contain the very interesting substances known as enzymes (lipase, for example) which induce hydrolysis; that is to say, they will cause any water present to disintegrate the fats (and other bodies) into simpler bodies. This may be facilitated by exposure to air and light, so that a freshly-expressed oil that is sweet may soon acquire an unpleasant taste and odor. In some cases we say it becomes

rancid, but in all cases the oil develops acidity, and the amount of the acidity of a particular oil is a function of time.

Under favorable conditions—and they are usually favorable—these changes take place within the oil-containing bodies, so that freshly-produced oil is usually acid, which acidity increases on keeping. The enzymes are "killed," or decomposed, or at least their directive activity ceases, when they have been exposed to a temperature of about 200° C. It has not been considered a good procedure by the practitioners of the art of oil extraction and refining, however, to heat the oil to such a temperature immediately after its production; but I venture the opinion that the increased development of acidity in crude oil in storage or in transit to a refinery will be materially affected by such treatment. However, it will be necessary to be assured that substances charred or scorched at that temperature are absent.

As mentioned above, oils and fats are primarily glycerides of the saturated palmitic ($C_{16}H_{32}O_2$) and stearic ($C_{18}H_{36}O_2$) acids, associated with the fatty acids of several unsaturated series. For example:

1. Oleic acid, $C_{18}H_{34}O_2$, type $C_nH_{2n-2}O_2$.
2. Linoleic acid, $C_{18}H_{32}O_2$, type $C_nH_{2n-4}O_2$.
3. Linolenic acid, $C_{18}H_{30}O_2$, type $C_nH_{2n-6}O_2$.
4. Clupanodonic acid, $C_{18}H_{28}O_2$, type $C_nH_{2n-8}O_2$.
5. Ricinoleic acid, $C_{18}H_{34}O_3$, type $C_nH_{2n-2}O_3$.

The last is an hydroxy acid, which undergoes a particular polymerization under suitable conditions.

Most fatty oils, on exposure to the air, tend to thicken, due partly to oxidation and partly to polymerization, or both. Oils are, in fact, classified by many according to their drying qualities and tendency toward resinification. These properties play an important part in their utilization in the arts; and their treatment in refining is materially affected by the time which may have elapsed from actual production to their refining. For example, a freshly-produced linseed oil may be profitably refined by a process which is inapplicable if the oil be "aged oil."

Oil, as stated, is normally a liquid, and we usually associate the phenomena of solution with a liquid. To be sure, this is a restricted conception, but will answer for our purposes. In this connection oil acts like water as a fluid. Water in motion carries

fine particles suspended through long distances and deposits them in time, when fairly quiet, as we know from the formation of alluvial soils. Water carries certain substances in solution. These latter substances are sometimes colored and are partly fixed on the filter when that water passes through certain filtering media. For instance, we are able to adsorb Congo red from a water solution with filter-paper. Again, water carries certain substances which do not stop on the filter; they are invisible and show themselves only when we apply the ultra-microscope. These finely-divided substances, not small enough to be in actual solution, will remain suspended in the water for long periods of time. They are called colloids. By various means, through heat, addition of an acid, an alkali, or a salt, by the influence of an electric current, or by the addition of other colloids, these very finely-divided substances may be caused to agglomerate; that is, they may be converted into particles of sufficient size to be separated from the fluid by means of a filter. Exactly the same is true of oils. Organic colloid solutions may be viscous; the liquid particles are suspended in a liquid medium.

Many of the contaminating substances, referred to here in general, may be suspended in the oil, may be in solution in the oil, or may be in a colloidal condition in the oil.

It will, therefore, be quite apparent that crude vegetable and animal oils contain a variety of impurities traceable to a great variety of causes. The character of the crude oil depends not only upon the kind and part of the vegetable (wood, nut, seed, etc.) and animal (fish, whale, etc.) used, but the quality of the raw material at the time of expressage or extraction (rusting, rotting, fermentation, sprouting, heating, etc.), the method followed, the care exercised in the process, and the conditions to which the oil is subjected prior to its refining. In many cases, in fact, we find metallic soaps present in the crude oil, which soaps have resulted from an interaction of decomposition products of the oil and the rendering vessels.

No universal method for refining animal and vegetable oils is known. Your forbearance will not be taxed, however, even were it profitable, in discussing all the various proposals for fitting these oils best to the several purposes experience and practice have shown them to be applicable. A number of processes have been proposed, patented, or kept secret during the last 125 years. Around the knowledge and power of the practical oil-refiner not a

little mystery still obtains. Each individual oil presents its own problem, and even the same oil by name, obtained under different conditions, involves judgment, based on the knowledge of the chemistry involved, to secure the best and most economical results. Furthermore, the use to which the oil is to be put must be considered; for example, one wants acid oil for some paints and neutral oils for foods.

Some four general methods for refining oils have been and are being worked in practice. They are:

1. Treatment with steam (plain or superheated) whereby some coagulation results and many odoriferous substances are driven off. This does not diminish the free fatty acid content of the oil so treated.

2. Treatment with variable amounts of concentrated sulphuric acid (Gower, 1792) under determined conditions of heat and agitation with or without air. The oil contains certain substances which, when flocculated by the acid and temperature, fall down and mechanically (a term used in several recognized authoritative books) carry down other impurities. This process does not diminish the acid content of the oil so treated.

3. Heating up under carefully-regulated temperature conditions with fullers' earth, bone-black, etc., and filtering. This process also yields an acid oil.

4. Adding caustic alkalies, or alkaline earths, of an amount and strength determined by laboratory experience (Barreswil, beginning nineteenth century), heating to the "break," settling and drawing off the oil, which floats upon the soap stock or "foots." This was supposed to give a neutral oil, but not until it had been washed several times with water.

Yet as late as last year a distinguished oil chemist, in a very interesting summary of the "Contributions of the Chemist to the Cotton-seed Oil Industry,"[1] said "the chemist . . . found that the quality of the oil followed the free fatty acid present." An empirical formula has been worked out to show this relationship to the free fatty acid. The rule is: Multiply the f. f. a. by 2 and add 4; that is, an oil showing 2 per cent. f. f. a. should give a shrinkage of 8 per cent. This is true only in a general way. I recently had a cotton-seed oil with 1.7 per cent. f. f. a., which

[1] *Journ. Ind. and Eng. Chem.*, 7 (1915), 277.

showed a shrinkage of 21 per cent. by the official method of the Cotton-seed Crushers' Association.

The writer quoted above further said "the chemist's greatest service to the industry has been in the refining of the oil . . ."

Wesson was here referring more especially to edible cotton-seed oil. In that connection, Lewkowitsch, the lamented Anglo-German specialist in oil chemistry and technology, has said:[2] "No chemically-treated oil or fat can be looked upon as a product fit for human consumption." I confess inability to comprehend this sharp distinction as to what is meant by a "chemical." Oxygen from a chromate is a chemical; oxygen of the air is not. Sulphuric acid is a chemical; caustic soda is not. It may be interjected here that certain statements transmitted by texts and sanctioned by law call for clarification and revision. No treatment of an oil or fat, which involves purification, rendering it palatable, agreeable to the sight, and avoids the introduction of constituents which may interfere with normal digestion should be forbidden. For fear of misunderstanding, it may be stated here that the method described below complies with all the most rigid laws of all nations and even the above-mentioned uneven discriminations.

An oil that is acid is unsatisfactory as a food. Acid oils corrode the vessels and generate objectionable gaseous products when used as burning fluids. Acid oils corrode the bearings when used as lubricants; so it is desirable to have neutral oils for many purposes. Yet a neutral oil does not "cut" into white lead, for example, so an acid oil is preferred as a paint vehicle; but Gardner has pointed out that the oil should not be too acid.

I have been more concerned with neutral oils and their production, so shall confine my remarks to preparation of that class of substances.

The present customary practice for refining vegetable oils referred to (the fourth mentioned above) depends upon neutralizing the free fatty acids in the crude oil usually by agitating the oil with an aqueous solution of an alkali, the strength and the amount having been previously determined by laboratory tests, agreed upon as a standard, and then heating the mixture during agitation to a suitable temperature until the oil "breaks." The mass is then allowed to stand until the "foots" settle to the bottom

[2] Vol. 2, p. 32, 3rd Edition.

of the kettle, when the supernatant oil is drawn off by means of a swivel siphon. According to the process of Chisholm, sodium silicate is added to facilitate the settling. Invariably some "dreg" floats on top of the oil. If this be very great its settling is sometimes facilitated by throwing salt on top of the oil in the kettle. The salt drags down some of the floating "dreg." In any event, the oil drawn off is clouded, perhaps on account of the presence of some dissolved soap or globulated moisture or suspended matter —all doubtless colloidal in nature. This oil is then "brightened" after drawing off by throwing in small amounts of fullers' earth, heating again, and passing through a filter-press. Sometimes, previous to this treatment with fullers' earth, the decanted oil is heated to 160° to 180° F. in a settling tank to cause the "foots" remaining in the oil to rise to the top, when it is skimmed off.

The time factor in settling (six to twelve hours) of the "foots" materially affects the completeness of the separation referred to above. Cocoanut oil sometimes requires forty-eight hours to settle. In any event, the "foots" is wet with oil. The "foots" also entrains oil. Consequently during the rush season the efficiency of yield of refined oil must be sacrificed for speed and quantity refined. In other words, the more speed in refining, the more loss of refined oil, whatever the analysis, upon which purchase and sale are based, may indicate.

A process which would reduce the amount of oil entrained in the "foots" to a minimum, thus increasing the yield of refined oil, and one which would not be dependent upon the slow subsidence of the "foots" (that is, admit of rapid separation with consequent increase in capacity of a refinery), therefore, seemed to me not only to be desirable, but, if secured, would approximate the highest efficiency one might hope for in such an industrial operation.

I have succeeded in working out such a process, and shall now proceed to describe the principles involved and at the same time demonstrate it to you as an analytical method. I have pleasure in exhibiting to you samples of the crude and refined (by my method) oils from a variety of sources.

The technical laboratory tests with batches of twelve to twenty pounds have been verified in the factory on a commercial scale. Some of the samples exhibited are from factory runs.

The aims to be accomplished are:

1. To reduce the amount of oil entrained in the " foots," thus increasing the yield of " whole oil."

2. To reduce the time of contact of the excess alkali (necessary for the " break " and to secure the best " color ") to the minimum.

3. A technological corollary calls for the utilization of any by-products.

It is to be assumed that all oils, good, bad, and indifferent, are to be treated. However, this may not be necessary, as in some cases only the good, and perhaps the indifferent, oils are refined under the old practice at some places. Certain foreign markets call for a highly-colored oil, so they do not present the problem of bleaching.

In my investigations, lasting through several years, I have taken various kinds of crude vegetable oils from various kinds of sources with various (extreme) conditions and refined them. In many cases I have been told that no attempt would ordinarily be made to refine a particular oil, as it should be sent to the soap-kettle, the corresponding price only being expected. Such oils would have represented much better values if they could have been refined by the usual practice. These oils in every case have yielded to my process, have been refined, and with a saving over the old processes. I may say, however, that China wood (tung) oil, castor oil, and aged linseed oil cannot be economically refined by the process. I wish also to repeat that I am referring to the production of neutral refined oils only.

If we can get the " foots " into such a condition that it may be filtered and then squeezed, we may reduce the amount of " whole oil " entrained.

If we can do this immediately after the " break " and while the oil is still hot, we shall be able to reduce the time the " whole oil " is exposed to the saponifying action of the excess alkali necessary to secure proper color, avoid the present practice of necessary " cleaning," and the second heating.

I have called your attention to the presence of bodies, which in general terms are called colloids, in oils. These colloids may or may not be colored; may or may not make the oil turbid. I have also shown that some colloids may be and are coagulated by heat, some by acids, some by alkalies, some by salts or electrolytes, and in time will settle out. Colloids that have been coagulated or lumped may be filtered out. Some coagulated colloids in their formation

adsorb coloring matter. The problem of economical filtration on the large scale necessary was one of great difficulty; in fact, so far as I am aware, it was unsolved previous to my investigation. Suitably-prepared cellulose fibre will adsorb some coloring matter. It will bring about an agglomeration of the material precipitated from oils by treating the oil with alkalies and heating, and it will bind the particles together so that they may lose their somewhat slimy character and then may be easily filtered away from the oil in which they were produced. Short-fibred "linters" or "delint" is a suitable form of cellulose for some oils.

Therefore I add cellulose, suitably prepared, along with the caustic to the oil to be refined. The "break" takes place normally on heating as in the ordinary process, but the precipitated mass is in such a physical condition that it may be separated from the oil immediately by filtration.

As mentioned above, some colloids, perhaps colored, are thrown down by salts, so in certain cases some salt (1 per cent. of sodium chloride) may be added. If there be a slight excess of water present, the sodium chloride serves also to "salt out" any soap in that water. The addition of salt, however, is not necessary in all cases.

I have also discovered that the tendency of the soaps formed by the caustic-alkali treatment to emulsify with the oil, or so to distribute themselves through the oil as to render their separation difficult, may be overcome by subjecting the oil, at a suitable stage of the treatment, to the action of an anhydrous salt which is capable of taking up water of crystallization, the perferred salt being dry sodium carbonate (soda ash), which, as is well known, is capable of taking up one, seven, or ten molecules of water of crystallization, according to temperature conditions. By such treatment the soaps which have already been formed by the treatment with caustic alkali, and which have become so incorporated with the oil as to be incapable of complete separation by ordinary filtration, are hardened or pectised, presumably by dehydration, and are so modified that they are readily separated by simple filtration. Sodium sulphate, which acts in the same way, may be used instead of soda ash.

The process is carried out by adding ordinarily 2 per cent. of prepared cellulose (less than 1 per cent. real cellulose) and a suitable amount of caustic soda (usually much stronger but

actually less in amount than is commonly used). The whole is thoroughly basted by mechanical means and then heated to 45° to 65° C. to produce the "break"; a determined amount of soda ash is added, after which it is filtered. At first some soap may pass through the filter-cloths. In that event, the first filtered oil may be run directly back into the refining kettle and pumped through the press until the oil is "bright." This usually occurs within a few minutes; in fact, the speed of filtration is directly dependent upon the speed of the pumps. This re-filtration also improves the color. This oil is neutral and can be deodorized and bleached, or both at once, or may be stored safely. If linters is used, ¼ to ½ per cent. of the dry cellulose is added.

These ideas are covered by four United States patents granted, Nos. 1,105,743, 1,105,744, 1,114,095, 1,130,698, and others applied for.

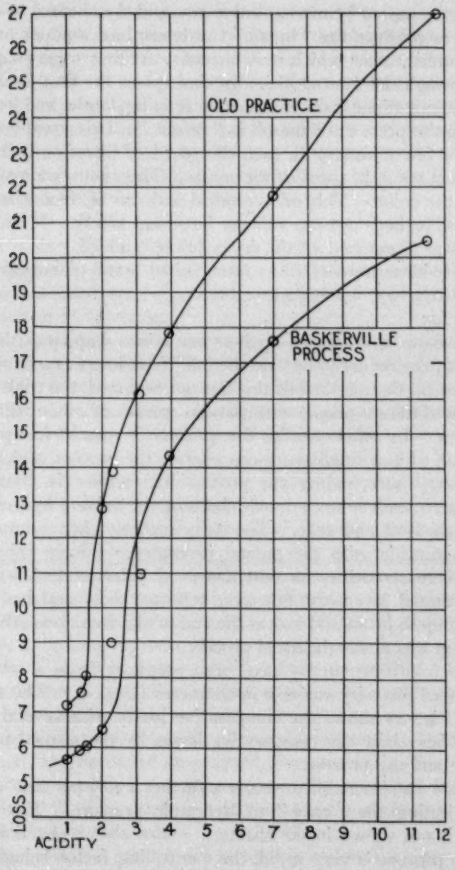
The danger of making a whole kettle into soap stock through failure of the refiner to be "on the job" is reduced to a minimum, as in several thousand trials this has not occurred, the trials being made by different people with various grades of oils of different character. In other words, the process is near "fool-proof." Any man of fair intelligence can operate the process, and the air of mystery surrounding the professional refiner is dissipated. The superintendent has a double check on the refinery by weighing the finished oil and cake. The daily reports when summed up should coincide with the annual inventory. I have known of cases where as much as 100,000 pounds of oil have failed to appear in the annual inventory, but were reported daily and had to be charged up to profit and loss at the end of the fiscal year when the operation was under the usual process.

The following curves have been prepared from a series of cotton-seed oils very variable in character (Fig. 1). The second chart (Fig. 2) shows the comparative losses with several other oils. They show the comparative losses by the normal present practice and my process.

I have also been able to secure a further 1 to 3 per cent. saving by subjecting the "cake" to hydraulic pressure. This extra saving is not shown in the charts.

The process is very rapid, the controlling factor being filter-press capacity. A study of plate filter-presses has indicated a preference for a centre-feed press making 1½- to 2-inch cakes.

FIG. 1.


OLD PRACTICE
BASKERVILLE PROCESS
LOSS
ACIDITY
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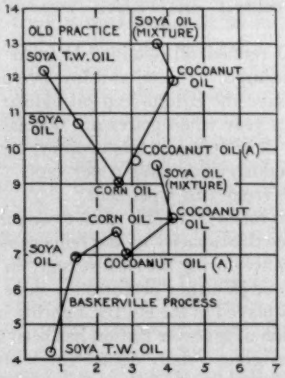
The filter-press problem in connection with the process is not one of filtering area, but cake capacity. Presses, as the Kelly or Sweetland, which are dumped mechanically, meet the conditions better than plate presses. A new Sweetland press recently devised for this process promises the best results. It is provided with bottom exits for the refined oil, and the under bivalve swings through an arc of 165 degrees. Monel metal filter-cloth makes the machine

FIG. 2.




practically permanent. By a slight increase in filter-press capacity the output of a refinery may be doubled or even tripled.

## UTILIZATION OF BY-PRODUCT.

The cake may be converted directly into soap, the cellulose becoming very finely comminuted. It is partially mercerized, partly converted into a colloid, and some of it forms an unobjectionable filler for some grades of soap, especially soap powders.

The cake may be "cut" with acid directly. The cellulose settles quickly in the aqueous layer from the black grease, which latter may be drawn off ready for market or use. When the cake is to be "cut," in order to reduce the amount of acid necessary, I prefer to use salt cake in place of soda ash as the "agglomerator."

A solution of nitre cake, the process of Dr. Jeffrey Stewart, of Philadelphia, patent assigned to the duPont de Nemours Company.

for the recovery of oil from soap stock, can also be used in cutting the cake. In view of the high price of acid at present, this may serve as an economical method for making "black grease."

Printed instructions for the use of the method in practice or as analytical procedure will be supplied to any who will write for them.

## SUMMARY.

A process has been worked out, based on scientific principles, for preparing neutral oils, which possesses the following advantages:

1. The actual refined oil obtained is from 1 to 10 per cent. more than now secured. Placed at a low average of 3 per cent., the process will save the cotton-seed oil industry in this country over $2,000,000 a year when prices are normal. The soja-bean oil industry, just developing in this country, can save 5 per cent. The peanut oil industry can save 6 per cent. The cocoanut oil industry can save from 3 to 5 per cent.

2. The process takes from one-tenth to one-third the time now necessary. Hence the capacity of the refinery is increased. This is of great importance during the rush season; in fact, its introduction will in economic efficiency perform the same rôle the tungsten filament lamp has played in the electric lighting industry, whereby the light production of a power station has been tripled.

3. The process gives a daily double check on the efficiency of the refinery.

4. The process is applicable to all grades of edible oils, which is not true with the common procedure.

5. Little new machinery is needed. The extra filter-press capacity called for will be more than paid for in the first year's profit.

6. The cost of chemicals is the same or less.

7. The by-product cake may be converted directly into a useful and commercial material.

THE COLLEGE OF THE CITY OF NEW YORK.

# PORTLAND CEMENT.*

BY

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PORTLAND cement may be defined as "the finely-pulverized product resulting from partial fusion of an intimate mixture of properly-proportioned argillaceous and calcareous materials."[1] When the fine powder is mixed with water a hard, stone-like mass is formed. The mortar thus obtained with Portland cement is far superior in strength and durability to any of the other various types of mortars commonly used in construction. This is due to the fact that Portland cement, which is the only cement formed by partial fusion of the raw materials, contains a compound known as tricalcic silicate, which is only formed at extremely high temperatures. The value of employing high temperatures in the manufacture of cement was discovered about one hundred years ago; it is only in recent years, however, that the process for the manufacture of Portland cement has been sufficiently developed so as to produce a uniform product on a large scale. Forty years ago its use was limited and it was manufactured only on a small scale; at the present time its use is so widespread that in 1915 it required over 90,000,000 barrels, costing over $125,000,000, to supply the demand in this country alone. This tremendous increase in production has been due to the increased use of Portland cement as a structural material, especially in concrete. The uses for concrete are many. It is used for the construction of sidewalks, roads, houses, dams, bridges, tunnels, forts, etc. In general, it may be said, therefore, that concrete is a substitute for stone. In some respects concrete is superior to stone as a building material, but under many conditions it is not so durable as the best building stone. One often sees a cement sidewalk which has disintegrated or hears of a concrete dam or bridge that is gradually going to pieces. There is reason to believe, however, that it may

* Presented at a meeting of the Section of Physics and Chemistry held Thursday, March 2, 1916.

[1] Standard Specifications, Am. Soc. Test. Materials, etc.

be possible to produce a cement which will yield a concrete of much greater durability than the Portland cement now made. Indeed, as the demand for Portland cement has increased and as the requirements of engineers have called for material of better quality, the manufacturers have been able to meet these demands and to improve continuously the quality of their product. This continuous improvement has been brought about almost entirely by improvements in the mechanical appliances and methods of the industry, and owes very little to new ideas of how to make Portland cement, based on a knowledge of what the product really is. And, in view of this fact that such progress has been possible under such circumstances, it would seem not unreasonable to look forward to further improvement in cement, now that its constitution has been definitely ascertained.

We now know that Portland cement is made up of a number of chemical compounds, and that of these compounds there is but one which in itself possesses all the properties of a desirable Portland cement. This compound, tricalcic silicate, makes up only about 35 per cent. of an average Portland cement. It would appear, therefore, that one method of increasing the strength and durability of Portland cement would be to increase the percentage of tricalcic silicate.

The early investigations which ultimately led to the production of cement containing tricalcic silicate may be said to have started from the desire of engineers to obtain a satisfactory cement which would harden under water. In order to discover such a cement, two distinct modes of attack were employed: the one, representative of the first investigations in England, was to proceed by more or less " hit-and-miss " methods to the determination of the proper substances to be used and of the methods employed for the manufacture of an hydraulic cement; the other mode of attack, which originated in France, was to proceed in a systematic manner and to make use of the knowledge of the chemistry of the substances available for such a cement.

While it is not our present purpose to take up an extended discussion of the relative merits of these two types of cement investigation, it may be well to give a brief account of the most important early investigations of each type, taking up first the researches carried on in England and then those of M. Vicat in France.

The cement industry may be said to have started in 1756 from the researches of John Smeaton, an English engineer. Smeaton [2] had been employed by Parliament to build a lighthouse upon a group of partially-exposed rocks in the English Channel. Two wooden structures had previously been built and each had experienced a comparatively short life. When Smeaton attacked the problem, he determined to build a structure which would weather the fiercest storms of the channel. One of the greatest difficulties he had to overcome was the failure of ordinary lime mortar to harden under water. In order that his foundations be firm it was necessary that some mortar be found which would meet this difficulty. To this end he undertook a series of investigations of lime mortars, the result of which was the discovery that a clayey limestone, when burned, produced a mortar which would not only harden better in air than ordinary lime but would also harden under water. Such a clayey limestone Smeaton found in Cornwall, and he made hydraulic lime by burning this stone. This hydraulic lime, when mixed with pazzolana, a pumice-like material of volcanic origin, produced a satisfactory mortar which Smeaton used in the construction of the Eddystone lighthouse. This cement of Smeaton's, while it was undoubtedly an excellent structural material, has never been widely used, for the reason that pozzolana is found only in a few volcanic regions, notably Italy, where it was previously used in the making of the famous old Roman cements.

This circumstance, that pozzolana was not found in England, led to further investigations to determine the possibility of making a satisfactory water cement without this ingredient. As a result of these investigations various processes for the manufacture of artificial Roman cements were patented. These so-called cements were really hydraulic limes, similar to that prepared by Smeaton, though they were made by burning limestone containing a rather higher percentage of clay. It was from one of these hydraulic limes, patented in 1824 by Joseph Aspdin, an English bricklayer, that Portland cement derives its name. Aspdin took out a patent for the manufacture of an improved cement, which he called Portland cement from its resemblance in appearance after hardening to Portland stone, a famous English building stone.

[2] John Smeaton, "Narrative of the Building, etc., of the Eddystone Lighthouse," chap. 5, Book VI.

This cement was made by heating together an intimate mixture of limestone and clay to a temperature sufficient to expel the carbon dioxide. The process thus described is incapable of producing a cement such as is now known as Portland cement, the temperature of burning not being sufficiently high for the formation of *the* essential constituent, tricalcic silicate. It was not long, however, before this defect became obvious, the value of burning to a temperature of incipient fusion being discovered in 1825. While the superiority of the cements thus made by partial fusion of the raw materials was soon recognized, the knowledge of why fusion is essential has but recently been discovered. We now know that it is tricalcic silicate which imparts to Portland cement its most valuable properties, and that it requires extremely high temperatures in order that this compound be formed from limestone and clay. In spite of this lack of scientific knowledge during the early stages of the development of the Portland cement industry in England, the proper proportions of limestone and clay to be used were discovered by burning various mixtures and testing the physical properties of the cements thus obtained.

The first scientific knowledge of the chemistry of cements resulted from various investigations carried on in France. Of these early researches, the most important are undoubtedly those of M. Vicat, who undertook to straighten out the chaos of opinions and opposing facts regarding cements which existed at the time he started his work in 1812. Without taking up the exact nature of the chaotic conditions, it may be briefly stated that Vicat made an attempt to determine: the relation between the quality of hydraulic lime and cement and the chemical composition of the stone whence they are derived; the nature of the chemical compounds formed during burning; and the changes which take place when the cement is mixed with water and hardens.

While he did not entirely accomplish his purpose, Vicat did evolve some very interesting theories as to the hardening of calcareous mortar and cements.

The theory which Vicat first adopted was that a portion of the alumina and silica of the sand being acted upon by the lime caused the mortar to harden by chemical combination. It was not long, however, before he discovered that even in mortars eighteen months old the hydraulic lime is without chemical action on the granitic sands, and, further, that there is no integral transforma-

tion of this lime into its carbonate. These facts led him "to inquire into the influence of a mechanical agency of the particles, either considered as the result of a mere interlacement, or as to the proper cohesion of the lime, in comparison with its adherence to the quartz or calcareous substance embodied by it."[3] Discarding the hypothesis of a mere interlacement as untenable, he proceeded to inquire into the possibilities of a cement matrix possessing the faculty of: (1) hardening without perceptible shrinkage; (2) hardening with perceptible shrinkage; each case being considered when the adherence is stronger than the cohesion, and *vice versa*. Considering each of these possibilities with reference to the available data on the mortars then known, Vicat concludes that the mortars of hydraulic limes are the only ones which cannot be explained by such a theory of aggregates.

Referring to the hardening of eminently hydraulic mortars, he says:[4] "We are therefore compelled to have recourse to other considerations; and most of the difficulties will at once disappear, if we consent to admit, first, that the action of adherence is not confined to a superficial effect or to contact, but that to a certain extent it augments the cohesion peculiar to the matrix; second, that the limits of this extent are the more enlarged, the more favorable are the circumstances in which the mixture is placed, to a continuance of the molecular movement which takes place in the gangue; third, that lastly, the increase of cohesion in the matrix is inversely proportional to the distance of its particles from the aggregated body which acts the part of the nucleus." Applying this theory, Vicat says:[5] "Is it contrary to the principles of science to suppose that the film of lime which attaches itself in adhesion to the surface of a hard body becomes itself a hard substance in respect to the film next to it, and that one after another these films may finally adhere to one another by an attraction superadded to the cohesion natural to them? Doubtless no; such an action may be kept up for a very long continuance, especially when the moist condition of the matrix favors it."

"The very remarkable experiments of Mr. Petot, Engineer of Roads, on the relations which exist between the solubilities of hydraulic lime joined with sand, and the proportions of mixtures,

[3] Vicat on Mortars and Cements (Trans. Cap. J. T. Smith), 288, p. 126.
[4] *Loc. cit.*, 307, p. 132.
[5] *Loc. cit.*, 308, p. 133.

leaves no doubt of the influence exerted by the presence of the quartz upon the cohesion of the lime."

Referring to this statement, J. T. Smith, who translated the works of Vicat, says (p. 134): "This observation seems to be confirmed by the result of some of my own experiments, although they were undertaken with quite a different view. In endeavoring to account for the absence of carbonic acid in mortars of great age, and in searching for the neutralizing power which had supplied its place in part, in depriving lime of its caustic quality, etc. . . ." The only ingredient which could produce this effect was, according to Smith, silica, although he was unable to obtain any direct proofs on which to found the assertion "that silica exercises a neutralizing power with lime in the humid way." He was able to show, however, "that silica has a strong affinity for lime in circumstances which may frequently occur in hydraulic cements; these are, when it (silica) is in a minute state of division, especially if gelatinous; a fact which is shown by its communicating to it (lime) the property of hardening under water, under circumstances in which the induration cannot be occasioned by absorption of the fluid, as in the setting of plaster of Paris and some other cements."

To return again to the work of Vicat, he found that "Rich lime, when lodged amongst the grains of quartz of an ordinary mortar, retains in it its characteristic properties, which are, to be soluble to the last particle in water and to remain soft for a great number of years when excluded from contact with air (carbon dioxide). When mixed, however, in certain proportions with an energetic pozzolana in a pulverulent state, the lime disappears in a way, becomes insoluble, and communicates to the compound the faculty of hardening in a short time, either in water or in inclosures impermeable to the air. Now in what way does this lime thus change its nature?"[6] After refuting previous theory, to the effect that the hardening is due to carbonization of the lime, Vicat concludes (paragraph 314): "We persist in thinking, as we have always maintained till now, that the lime in cements of natural or artificial pozzolanas, etc., enters into chemical combination with these substances. Our opinion harmonizes with numerous facts set forth in the course of this work. These facts,

[6] *Loc. cit.*, 311, pp. 135–136.

it is true, cannot be looked upon as direct proofs, but we know that in matters of this kind direct proofs are extremely difficult and sometimes impossible to obtain; we know, moreover, that geometricians consider two straight lines to be equal, when they have proved that one can neither be smaller nor larger than the other."

In this manner Vicat ended his very valuable treatise on mortars and cements. The few scattered quotations from this work which are given here may appear to be rather incoherent, but they contain many ideas and suggestions which are extremely useful to those interested in the production of a Portland cement far superior to that now made. It is true that the cements which Vicat prepared and studied are inferior and have little resemblance to present-day Portland cement; even so, the fundamental theories of cement making which he advanced have not been refuted up to the present time and appear as applicable to Portland cement as to Vicat's hydraulic limes and cements.

These theories of cement making, which one must infer Vicat had in mind though he embodied them in no simple direct statement, are: (1) that the lime contained in cement mortars should be present in chemical combination with some material other than water; (2) that this other material should be silica, preferably in a finely-divided or gelatinous condition.

Later in this paper, after having presented our present knowledge of the constitution of Portland cement and of the chemistry of the hardening of mortar, an attempt will be made to show that Vicat's theories not only explain in a measure the essential active principle of the hardening of Portland cement mortar, but also indicate that it should be possible to produce a cement which will in turn produce a mortar of much greater strength and durability.

While Vicat, in France, was working out these theories as to the best cement practice, the English, with little or no theoretical knowledge (more by luck than otherwise), discovered a process for the production of an hydraulic cement far superior to any then produced in France. This discovery, of which a brief account has already been given, was, from one point of view, rather unfortunate, for the reason that it yielded a cement (Portland cement) so far superior to any previously known that apparently the idea became fixed—and to some extent still prevails—that there

is no possibility of producing a still better cement. It would appear that this minimized to some extent the recognition of the value of theoretical cement investigation, since but little of value was undertaken for some time after Vicat's investigations.

In spite of this fact, however, that but little has been known of the theoretical possibilities involved in the chemistry of the process, the many merely mechanical improvements have made possible the production of a better and more uniform product than was first made.

At first the English and later the German process produced cement which was the standard of quality; to-day, however, the best Portland cement is undoubtedly made in America. This has been brought about by improvements in the mechanical appliances of the industry which have been developed largely in this country and which, as we now know, have gradually increased the percentage of tricalcic silicate in cement by affording more favorable conditions for the formation of this compound.

Portland cement is ordinarily prepared by heating together a mixture of two raw materials, one composed largely of calcium carbonate, the other of aluminum silicates. The most typical materials answering to this description are limestone and clay, both of which occur in Nature in great quantities and in a number of varieties; other materials sometimes used are blast-furnace slag with limestone. Any combination of raw materials containing lime, alumina, and silica—the essential components—in the proper proportions may be used, however.

Briefly outlined, the method commonly used in America for the manufacture of Portland cement is as follows: The raw materials —namely, limestone and clay, or their equivalents—are crushed and dried, in order to insure satisfactory grinding and mixing; they are then mixed in the desired proportions, as indicated by previous chemical analysis, ground together until the whole of the material is reduced to very fine powder, and burned. The burning is carried out in a rotary kiln, the action of which is continuous, the raw material entering at one end and the cement clinker passing out at the other. These kilns are cylindrical, ranging from 60 to 150 feet in length and 5 to 8 feet in diameter, and are built up of steel plates lined with highly refractory material; they are supported in a slightly-inclined position by friction rollers and are slowly rotated. The fuel commonly used is

bituminous coal, which, after being thoroughly dried and powdered, is blown by compressed air into the lower end of the kiln, thus securing very thorough combustion. This arrangement insures the maintenance of a high temperature at the lower end of the kiln, so that the raw material passing down encounters a continually-increasing temperature. The changes taking place in the progress of the material through the kiln may be divided into three stages: in the first the material is thoroughly dried, in the second all organic matter is destroyed and the carbon dioxide of the calcium carbonate is expelled, while the third is the chemical reaction between the lime, alumina, and silica to form the clinker. The time of passage through the kiln is about one and one-half hours, and the final temperature is about 1425° C. The clinker, in the form of granules varying in size from that of a pea to that of a large marble, is a partially-fused mass of the chemical substances formed by the reactions occurring in the third stage; when ground to a fine powder, it constitutes the Portland cement of commerce. It is usual, however, to mix with the clinker, before it is ground, a small proportion of gypsum, the purpose of which is to regulate the time of setting of the cement when mixed with water.

It has just been stated that Portland cement clinker is the result of chemical combination of the three oxides, lime, alumina, silica; but beside these three—which are the essential components—two others, namely, magnesia and ferric oxide, always occur to some extent in commercial cement. The average of a large number of chemical analyses of American-made Portland cement is, according to Meade:[7]

| | | | |
|---|---|---|---|
| CaO ..... | 62.0 per cent. | $Fe_2O_3$ ..... | 2.5 per cent. |
| $Al_2O_3$ ..... | 7.5 per cent. | MgO ..... | 2.5 per cent. |
| $SiO_2$ ..... | 22.0 per cent. | $SO_3$ ..... | 1.5 per cent. |

From this it is evident that more than 90 per cent. of an average Portland cement consists of the three oxides, CaO, $Al_2O_3$, $SiO_2$; one would expect, therefore, that its properties are due mainly to the presence of the above three components, and that the relatively small admixture of the other oxides exerts at most a wholly secondary influence. Indeed, it has been shown that good Portland

[7] R. K. Meade, "Portland Cement," p. 30.

cement can be made from the three pure oxides, lime, alumina, and silica, in the proper proportions.

Now, ordinary chemical methods enable us to ascertain the aggregate proportion of each oxide present, but they yield us no information as to the manner in which these oxides are combined with one another—in other words, as to the substances which actually are present in the clinker and are responsible for its characteristic properties. The determination of this question is very important, for this reason; that, until we know what these substances actually are, we cannot hope to improve the quality in any desired direction, except by cut-and-try methods; and it is generally recognized that such empirical methods are much less certain, and take a vastly longer time to reach the goal, than methods based on a real knowledge of the factors in the problem. The determination of this question has been the object of a very large number of investigations; but the experimental basis of most of this work has been altogether insufficient to decide the several questions at issue. There has been in general a failure to realize the fact that a system so complicated as this can be unravelled only by proceeding systematically, using as a guide the principle known as the phase rule and establishing definite criteria for the recognition of the several substances which occur.

Cement clinker is a mixture of substances of very similar properties, and is, moreover, exceedingly fine grained, as a consequence of which it is a matter of some difficulty to make quantitative determinations of the constituents; but this difficulty can be surmounted by studying separately each of the presumable constituents of the clinker and determining definite values of certain properties which serve to characterize it and to distinguish it from other possible constituents. Accordingly the first problem is to isolate and determine all the possible compounds of lime, alumina, and silica which we may expect to find in Portland cement clinker, to establish their relations at high temperatures, and to ascertain their optical characteristics which constitute the most convenient and satisfactory criterion of the identity of the several substances.

These characteristic properties of the several solid substances, containing only CaO, $Al_2O_3$, $SiO_2$, which are likely to occur in Portland cement have been determined at the Geophysical Laboratory of the Carnegie Institution in Washington in the course of a systematic investigation of all compounds formed when any mix-

ture of these oxides is heated to a high temperature. In American-made Portland cements the relative proportions of these oxides vary only between comparatively narrow limits: CaO, 60 to 64; $Al_2O_3$, 5 to 9; $SiO_2$, 19 to 25; in other words, in considering this special problem we have to deal with a very restricted portion of the field of the whole system $CaO - Al_2O_3 - SiO_2$.

### THE TERNARY SYSTEM $CaO-Al_2O_3-SiO_2$.

In order to work out this system completely it proved necessary to investigate about 1000 different mixtures of these three oxides and to make about 7000 heat treatments and microscopical examinations of the resultant products. Each such mixture, which was always made up of especially pure materials, was alternately fused and ground to a fine powder, the fusions being made in a platinum crucible to avoid contamination, in order to obtain a thoroughly-combined product. Each of these products was heated in an electric furnace, the temperature of which was carefully controlled and measured, until all changes had ceased, when it was quickly chilled; and the resultant material was subjected to a complete optical study. This procedure, which was carried out systematically, enables one to determine the crystalline phases present at temperatures ranging from that at which melting begins to that at which the charge is completely melted; and thus to ascertain the melting temperature and optical properties of all compounds of lime, alumina, and silica which form when any mixture of these three oxides is heated.

Before taking up the discussion of the application of the results thus obtained to the study of Portland cement clinker, a brief description, illustrated with photographs (Figs. 1 to 6) of the apparatus employed in this investigation, is given.

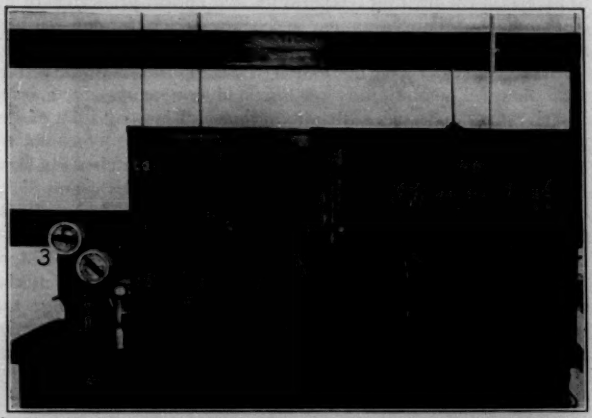
Fig. 1 is a photograph of a battery of three Fletcher gas-blast furnaces in which the various mixtures of CaO, $Al_2O_3$, and $SiO_2$, contained in platinum crucibles, were fused. Three of the platinum crucibles used are shown in the foreground.

The crushing and grinding apparatus employed for the reduction of the fused material to a fine powder is shown in Fig. 2; the steel mortar and pestle being used for preliminary crushing; the battery of mechanical agate mortars for further crushing and grinding; and occasionally, when extremely fine powder was

FIG. 1.

Battery of three Fletcher gas-blast furnaces used for fusing mixtures of CaO, $Al_2O_3$, and $SiO_2$ in platinum crucibles.

FIG. 2.




Crushing and grinding apparatus for the reduction of clinker to a fine powder: (1) steel mortar and pestle; (2) battery of mechanical agate mortars; (3) porcelain ball mills.

desired, the material was subjected to the pulverizing action of the porcelain ball mill.

The general arrangement of the apparatus used for the isolation of the different crystalline compounds and for the determination of melting temperatures up to 1625° C. is shown in the photograph (Fig. 3). The essential features of this apparatus are the

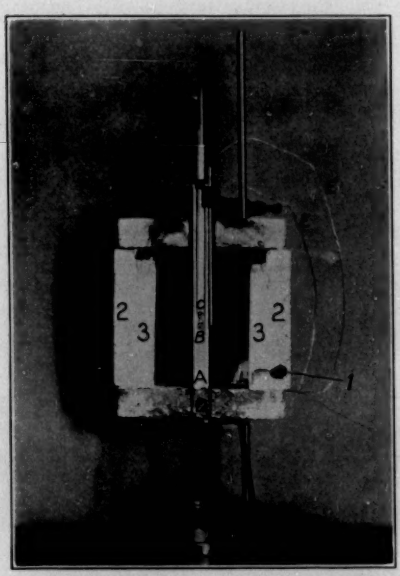
FIG. 3.

Photograph to show general arrangement of electric furnaces and temperature measuring device used for the determination of melting-points and for the isolation of the constituents of clinker: (1) platinum wire electric resistance furnaces; (2) Pt-Rh thermo-element; (3) electrical connection from thermo-element to galvanometer-potentiometer installation; (4) galvanometer; (5) potentiometer; (6) resistance for furnace temperature control.

platinum furnace and the temperature measuring device. The platinum furnace consists of a coil of platinum wire (wire 1.2 mm. diameter; coil 2½ inches diameter, 9 inches long, six turns to the inch) wound on the inside of a cylinder of impure magnesite which is insulated with MgO powder and a fire clay cylinder. Temperatures within the platinum furnace are measured with a platinum-rhodium thermo-element, in connection with a potentiometer and

galvanometer.[8] It is heated by the current from a storage battery (voltage 110, capacity 300 ampère hours), and the temperature within the furnace can be maintained constant (+2°) at 1550°

FIG. 4.




Cross-section of platinum quenching furnace: (1) platinum wire heating coil; (2) fire-clay shell of furnace; (3) highly refractory material for heat insulation; *A*, porcelain tube passing through centre of furnace; *E*, thermo-element; *B*, clinker wrapped in platinum foil; *C*, porcelain ring, suspended by fine platinum wire; + and −, heavy platinum wire leads; *D* removable plug; *F*, beaker of mercury.

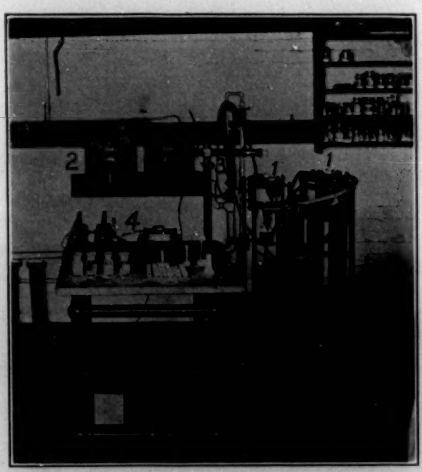
for a period of 12 hours; for lower temperatures the temperature can be maintained constant for much longer periods of time.

The photograph (Fig. 4) shows a vertical cross-section of a

[8] Walter P. White, "Potentiometer Installation, Especially for High-temperature and Thermo-electric Work," *Phys. Rev.*, XXV, 334–352 (1907).

platinum furnace fitted up with a quenching device. This device consists of a porcelain tube *A* passing through the furnace. On the outside of this tube the thermo-element *E* is fastened. The charge is contained in platinum foil *B*, suspended by a small porcelain ring from the fine platinum wire *C*. This wire is attached to two heavy platinum leads marked + and —. The tube is closed at the bottom by the removable plug *D*. *F* is a dish of

FIG. 5.

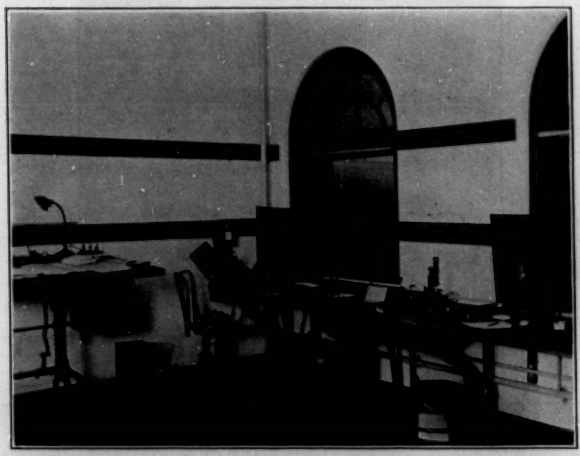



Photograph to show arrangement of iridium furnaces and optical pyrometer: (1) iridium furnace tubes within highly refractory shells; (2) electrical resistance for temperature control; (3) optical pyrometer; (4) ammeter for indicating temperature.

mercury. In operation the charge is brought to the desired temperature and held for a suitable length of time. The plug *D* is removed and a strong current passed through the wire *C*. The current fuses the wire, dropping the charge into the vessel *F*. The porcelain ring *C* prevents the wire of *B* from sticking to the suspending wire at *C*. The operation of the quenching device thus described enables one to quickly chill a small charge of material which has been heated to any temperature up to 1625° C.

For temperatures above 1625° C. no satisfactory quenching device or furnace has yet been devised for the study of mineral oxides. In such a furnace it is essential to maintain an oxidizing atmosphere and a fairly constant temperature which can be measured. Conditions approaching these requirements can be maintained in the iridium furnace, but no suitable refractory materials for the construction of a quenching device in this furnace are known. The iridium furnace consists of a straight iridium tube

FIG. 6.



Photograph to show arrangement of microscopes used for the study of constituents of clinker.

about 18 cm. long and 4 cm. in diameter, and is heated by a low-voltage alternating current. Temperatures within this furnace are measured with an optical pyrometer.[9] This furnace is used only for the determination of melting-points of substances which melt completely at a definite temperature within the range of

[9] Day, Shepherd and Wright, "Lime-Silica Series of Minerals," *Am. Jour. Sci.* (4), xxii, 286, 1906.

1625° – 2100°. A photograph to show the general arrangement of the iridium furnace, with device for temperature control and the optical pyrometer used for the measurement of temperature in this furnace, is given as Fig. 5.

Fig. 6 is a photograph showing the microscopes used for the optical study of fused mixtures after being quenched from various temperatures.

Having shown the general method of attack and the nature of the apparatus employed in this investigation of CaO, $Al_2O_3$, and $SiO_2$, let us now consider the results obtained.

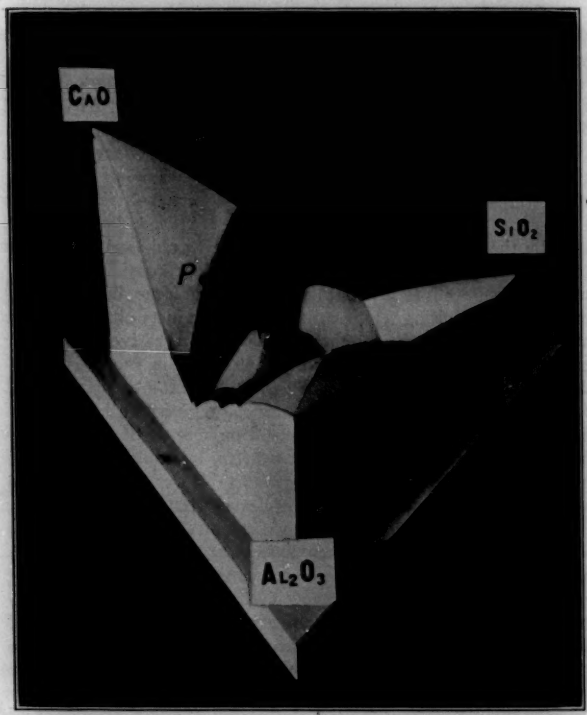
The data can be interpreted most readily if they are plotted in three dimensions; the concentration (composition) of each mixture is represented by a point within an equilateral triangle[10] on the horizontal plane, the magnitude of the corresponding temperature by the distance above this plane. It would lead us too far to go into details of the construction and properties of such a model;[11] suffice it to say that the series of surfaces thus described represent the melting temperatures of all products obtained when any mixture of the three oxides is heated progressively to higher and higher temperature. A photograph of such a model is reproduced in Fig. 7. As can be seen from the photograph, the model resembles a relief map of a mountainous region; each mountain peak is the melting-point of a pure component or of a pure compound; the mountain slopes represent the melting temperatures of a component or compound in ternary mixtures (each mountain slope in Fig. 7 is shaded in order to clearly define its boundaries); the points where the rivers in the valleys meet to form a lake are the lowest melting temperatures, known as eutectic points. This model, when interpreted with the aid of the principles underlying such equilibria, enables one to specify the order in which the several crystalline substances will appear when any melt composed entirely of lime, alumina, and silica is slowly cooled, and also to state what are the final products when any such melt has completely crystallized.

[10] In such a diagram, the pure components CaO, $Al_2O_3$, and $SiO_2$ are represented by the apices of the triangle; the binary systems CaO–$Al_2O_3$, CaO–$SiO_2$ and $Al_2O_3$–$SiO_2$ by the sides of the triangle, and ternary mixtures by points within the triangle.

[11] Those interested in the details of all this work are referred to previous papers, particularly Rankin and Wright, *Am. J. Sci.* (4), 39 (1915), 1, 79; and G. A. Rankin, *J. Ind. Eng. Chem.*, 7, 466 (1915).

Let us consider the crystalline substances which will separate from a melt composed only of these three oxides in the proportions

FIG. 7.

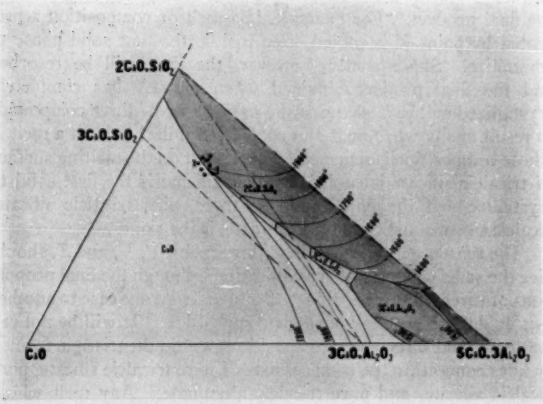



Photograph of solid model of concentration-temperature diagram of the ternary system $CaO$–$Al_2O_3$–$SiO_2$. Black dot *P* gives composition and melting temperature of pure Portland cement clinker.

such that they will produce a good Portland cement. For this purpose a diagram such as Fig. 8 is useful. This diagram is a projection on the horizontal plane of that portion of the solid

model necessary for our present purpose. The corresponding temperatures are here represented by isothermal lines, which are completely analogous to the contour lines on an ordinary map. The shaded areas correspond to the surfaces of Fig. 7. In this diagram the group of dots which represent mixtures of CaO, $Al_2O_3$, and $SiO_2$ from which Portland cement of good quality can be made correspond to the circle in solid model, Fig. 7. It will be seen that some of these dots represent points on the fusion

FIG. 8.




Projection of a portion of concentration-temperature solid model of system $CaO$–$Al_2O_3$–$SiO_2$, with isotherms. The dots represent mixtures of CaO, $Al_2O_3$, and $SiO_2$ from which Portland cement of good quality can be made.

surface of dicalcic silicate, others on the fusion surface of pure CaO, and still others, points on the fusion surface of tricalcic silicate.

If now a melt whose composition is represented by point *P* on the surface for dicalcic silicate is cooled, it is evident that this compound will crystallize at a temperature of about 1900° C. On further cooling dicalcic silicate will continue to crystallize alone until a temperature of about 1800° C. is reached, when tricalcic silicate will begin to crystallize. These two compounds,

dicalcic silicate and tricalcic silicate, will now crystallize together until, when the temperature of the cooling melt has reached 1455°, tricalcic aluminate appears. At this temperature the melt will crystallize completely, and the final product thus obtained will be made up of the compounds, dicalcic silicate, tricalcic silicate, and tricalcic aluminate.

The composition of the melt which when crystallized gives this product, it will be remembered, is that of point $P$ on the melting surface of dicalcic silicate. If now a melt whose composition is represented by a point on the melting surface of CaO or tricalcic silicate is cooled, the same group of substances will be present in the final product. For example, if a melt of composition represented by point $X$ is cooled, lime will be the first solid phase to crystallize. Subsequently, however, the lime will be resorbed and the final product obtained when melt $X$ has completely crystallized will be made up of the same group of three compounds as result finally when melt $P$ is cooled. Similarly, when a melt $Z$ whose composition is represented by a point on the melting surface of tricalcic silicate is cooled, tricalcic silicate is the first solid to crystallize, but the final group of three, viz., tricalcic silicate, dicalcic silicate, and tricalcic aluminate, is the same.

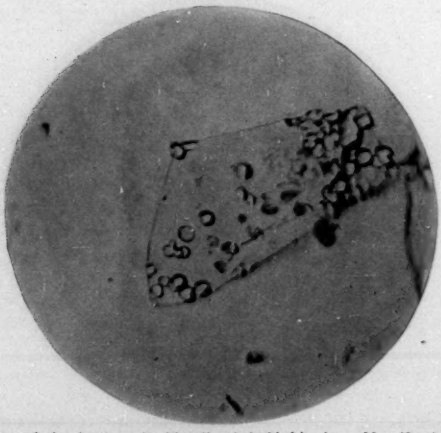
The reason why each of these three melts, $P$, $X$, and $Z$, should give the same products of crystallization—though the final proportions of three substances differ, of course, from one case to another—is evident if we consider their composition. It will be noticed that $P$, $X$, and $Z$ represent compositions within the triangle formed by lines connecting the compositions of pure tricalcic silicate, pure dicalcic silicate, and pure tricalcic aluminate. Any melt whose composition is represented by a point in this triangle, when slowly cooled, will yield a final product made up of these three compounds; so that, while the order in which these compounds crystallize from the melts $P$, $X$, and $Z$ respectively is different, the nature of the final product of crystallization is in each case necessarily the same.

Now the points $P$, $X$, and $Z$, in accordance with the statement on page 761, represent mixtures of CaO, $Al_2O_3$, and $SiO_2$ such that each will yield a good Portland cement when properly burned. We have now determined the compounds which will be formed when such mixtures are melted and slowly cooled. While Portland cement is not manufactured in this way, still the product

resulting from the crystallization of the completely-melted material is a good Portland cement, and the determination and identification of the constituents are more readily carried out.

In the actual manufacture of Portland cement, the necessary compounds are formed by burning at a temperature much below that required for complete melting. If, however, the cement clinker is not perfectly burned (the necessary compounds are not completely formed) there will be present, besides the three com-

FIG. 9.



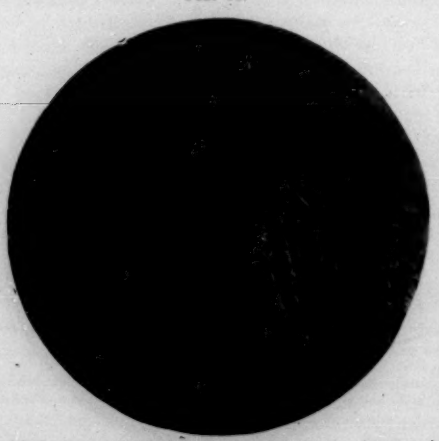
Photomicrograph showing crystals of free lime imbedded in glass. Magnification, × 150.

pounds already mentioned, two others; namely, CaO and the compound $5CaO.Al_2O_3$.

The major constituents of Portland cement clinker made up only of the oxides CaO, $Al_2O_3$, and $SiO_2$ are, therefore, the three compounds $3CaO.SiO_2$, $2CaO.SiO_2$, and $3CaO.Al_2O_3$. The compound $5CaO.3Al_2O_3$ and CaO are minor constituents. Each of these compounds has optical properties peculiar to itself which serve to distinguish it from the rest. The several characteristic optical and crystallographical properties were obtained by a study of each compound by itself. These values are constants for the

individual compounds in all mixtures made up from pure CaO, $Al_2O_3$, and $SiO_2$; *i.e.*, the final products resulting when such mixtures are heated are present as individuals of constant optical properties and not as solid solutions. Photomicrographs, to show each of these constituents as isolated crystals, are given in Figs. 9 to 16. These crystals, which are shown here as they occur imbedded in fragments of glass, were thus obtained by the quench-

FIG. 10.*



Photomicrograph showing crystals of tricalic aluminate imbedded in a fragment of glass. Magnification, × 150.

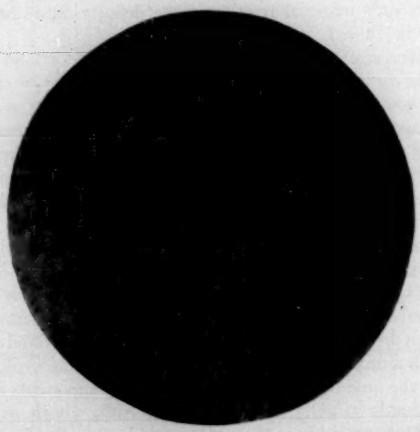
*This photomicrograph of crystals of $3CaO.Al_2O_3$ shows an effect which is commonly observed in "quenchings" which contain a crystalline material which crystallizes very rapidly in a cooling melt. This effect, which is due to inability to prevent crystallization taking place during the quenching process, is shown here by the fine fringe surrounding the crystals which were present in the liquid (glass) before quenching.

ing method already described. It will be noticed that, except for the $3CaO.SiO_2$, the other constituents obtained in this way do not show any definite crystalline outline, but that they appear as more or less indistinct, irregularly-shaped grains in the fragments of glass. In spite of this, the fact that each of these grains is isolated in glass (surrounded by a medium of uniform optical character) enables one to determine its characteristic optical

properties. While it is not possible to show all of the optical characteristics of each constituent by photographs, it is possible to thus show certain of these characteristics.

Figs. 9, 10, and 11 represent crystals of lime, tricalcic aluminate, and the compound $5CaO.3Al_2O_3$, respectively, imbedded in fragments of glass. These three compounds are optically isotropic, so that it is not possible to show here the most characteristic distinguishing property of each of these compounds,

FIG. 11.



Photomicrograph showing crystals of the compound $5CaO.3Al_2O_3$ imbedded in a fragment of glass. Magnification, × 150.

namely, the value of its refractive index. Also, since they are isotropic, they are inactive toward polarized light, and so photomicrographs taken with the nicols crossed show simply a black field (Fig. 12).

Figs. 13 and 15 show crystals of dicalcic silicate and tricalcic silicate, respectively, imbedded in fragments of glass. Figs. 14 and 16 are the same, except that the photomicrographs were taken with the nicols crossed. This shows something as to the action of polarized light toward these compounds, dicalcic silicate and

tricalcic silicate, which are optically birefracting. It is not possible, however, to show photographically the exact difference in the birefringence of these two compounds, the birefringence of tricalcic silicate really being very weak as compared with that of dicalcic silicate.

These photomicrographs of the constituents of Portland cement, while they thus show something as to the optical nature of these compounds, are not sufficient for their certain identification, especially as they occur in fine-grained mixtures of the nature of Portland cement clinker. The identification of these compounds in such material requires more definite data, such as is contained in Table I.

Microscopical examination of commercial Portland cement clinker shows it to be made up largely (over 90 per cent.) of the three compounds, $2CaO.SiO_2$, $3CaO.SiO_2$, and $3CaO.Al_2O_3$. It would appear, therefore, that the value of Portland cement as a cementing material when mixed with water is largely due to one or more of these compounds. Before taking up the cementing value of each of these compounds, however, let us consider their formation when Portland cement is burned.

For this purpose let us follow the reactions which take place when a mixture whose composition is CaO (as $CaCO_3$) 68.4 per cent., $Al_2O_3$ 8.0 per cent., and $SiO_2$ 23.6 per cent. is slowly heated. This mixture made up only of the pure oxides lime, alumina, and silica, when properly burned, will produce a good Portland cement. When such a mixture is heated the first change is the evolution of the $CO_2$; the lime then unites with the other components to form the compounds $5CaO.3Al_2O_3$ and $2CaO.SiO_2$ (both of which form readily), probably in the order named, since the former has a lower melting-point than the latter; subsequently these two compounds unite in part with more lime, and the compounds $3CaO.Al_2O_3$ and $3CaO.SiO_2$ appear. This formation of the last two compounds—a process which goes on very slowly in mixtures of their own composition—is materially facilitated by the circumstance that in the ternary mixtures a portion of the charge has already melted and promotes reaction by acting as a flux or solvent. The temperature at which this flux first appears is 1335° C., the eutectic temperature for the three compounds $2CaO.SiO_2$, $5CaO.3Al_2O_3$, and $3CaO.Al_2O_3$. As the temperature of burning gradually rises above 1335° the relative amount of flux increases

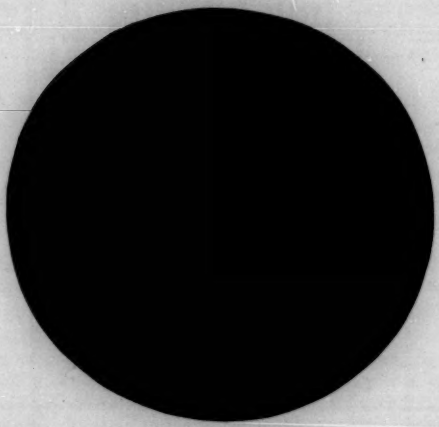
TABLE I.

*Optical-Crystallographical Properties of the Compounds Present in Portland Cement Clinker.**

| Composition | Crystal system | Crystal habit | Cleavage | Hardness | Elongation | Optical orientation | $\alpha$ | $\beta$ | $\gamma$ | Optical character | Optic axial angle | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CaO | isometric | unmodified cubes | perfect (100) | 3–4 | .. | ..... | .... | .... | 1.83 | .. | ..... | Crystals often show optical anomalies. |
| $\gamma$-2CaO.$SiO_2$ | probably monoclinic | prismatic | g (001)<br>g (100) | ...<br>... | $\gamma$<br>$\alpha$ | $b=\beta$<br>$c:\gamma=3°$(?) | 1.642 | 1.645 | 1.654 | – | $2E=52°$ | Obtainable only as fine powder. Plane of optic axes normal to cleavage direction. |
| $\beta$-2CaO.$SiO_2$ | orthorhombic or monoclinic | irreg. grains prisms | poor | 5–6 | ... | ..... | 1.717 | | 1.735 | + | large | Plane of optic axes paralleltoelongation. |
| $\alpha$-2CaO.$SiO_2$ | monoclinic or triclinic | irregular grains | | 5–6 | ... | $c:a'=18°$ | 1.715 | 1.720 | 1.737 | + | large | Intricate polysynthetic twinning is characteristic of this form. |
| $\beta'$-2CaO.$SiO_2$ | ..... | equant gr. | | ... | ... | ..... | .... | .... | 1.715 | + | small or uniaxial (?) | Birefringence very weak. |
| 3CaO.$SiO_2$ | monoclinic (?) | equant grains | ..... | ... | ... | $c=\gamma$ | .... | .... | 1.715 | – | small or uniaxial | Birefringence very weak. Twinning lamellaenotuncommon. |
| 3CaO.$Al_2O_3$ | isometric | equant grains | p (111) or p (110) | 6 | ... | ..... | .... | .... | 1.710 | | ..... | Occasionally gray interference colors appearasresultofstrain. |
| 5CaO.3$Al_2O_3$ (stable) | isometric | equant grains | fibers | 5 | ... | ..... | .... | .... | 1.608 | | ..... | Stable form. |
| 5CaO.3$Al_2O_3$ (unstable) | probably orthorhombic | fibers prisms | p. prismatic | 5 | $\alpha$ | ..... | 1.687 | | 1.692 | – (?) | large | Plane of optic axes parallel with fiber elongation. |

* This table is a portion of that giving optical properties of all compounds of CaO, $Al_2O_3$ and $SiO_2$ as determined by F. E. Wright and published in *Am. Jour. Sci.*, [4] 39 (1915), 74–75.

FIG. 12.

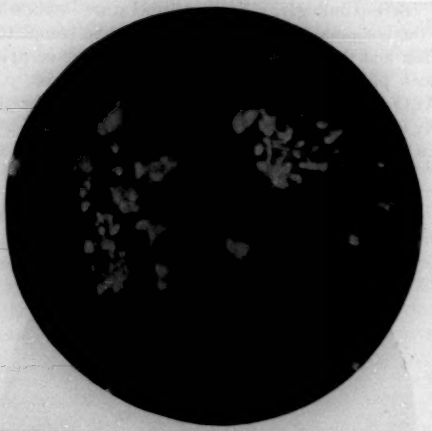


Photomicrograph, with nicols crossed, of either lime, tricalcic silicate, or $5CaO.3Al_2O_3$ imbedded in glass.

FIG. 13.

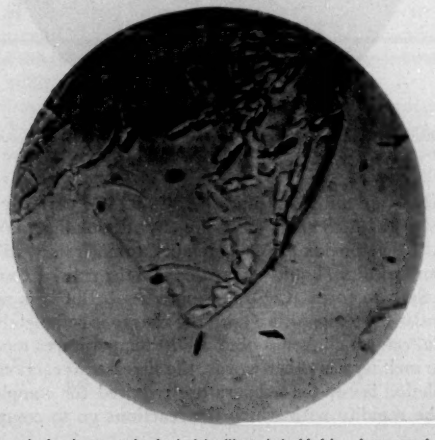
Photomicrograph showing crystals of dicalcic silicate imbedded in fragments of glass. Magnification, X 150.

FIG. 14.



Photomicrograph taken with crossed nicols, showing crystals of dicalcic silicate imbedded in fragments of glass. Magnification, × 150.

FIG. 15.



Photomicrograph showing crystals of tricalcic silicate imbedded in a fragment of glass. Magnification, × 150.

and the rate of formation of $3CaO.Al_2O_3$ and $3CaO.SiO_2$ increases correspondingly. At a temperature somewhat above 1335° the compound $5CaO.3Al_2O_3$ will have completely melted in the flux and the formation of $3CaO.Al_2O_3$ is complete. The substances present as crystals at this stage are $3CaO.SiO_2$, $3CaO.Al_2O_3$, $2CaO.SiO_2$, and free CaO. Of these the $3CaO.SiO_2$ is rapidly *increasing* in amount, due to combination of $2CaO.SiO_2$ with CaO, while the amounts of solid $2CaO.SiO_2$, CaO, and

FIG. 16.

Photomicrograph taken with crossed nicols, showing crystals of tricalcic silicate imbedded in a fragment of glass. Magnification, × 150.

$3CaO.Al_2O_3$ are all decreasing, the $2CaO.SiO_2$ partially by combination with CaO and partially by dissolving along with $3CaO.Al_2O_3$ in the flux. As the temperature is raised still further the amount of flux (liquid) increases and the rate of combination of $CaO.SiO_2$ to form $3CaO.SiO$ increases. But it is not necessary to raise the temperature until the charge is completely melted, as normal cement clinker is obtained at temperatures much below complete melting; in other words, the necessary reactions will go to completion below the temperature required for complete melting. The rapidity with which the reactions go to completion is

governed by the temperature and by the amount of the flux formed at that temperature. The requisite amount of flux, in turn, depends upon the fineness of the raw materials, since the finer these materials are ground the more readily the components will combine. For finely-ground raw materials of the above composition, composed only of CaO, $Al_2O_3$, and $SiO_2$, a temperature of about 1650° C. is required for burning. At this temperature the clinker would be about 30 per cent. melted and 70 per cent. solid crystalline material, a proportion of flux which would admit of the necessary reactions going to completion in a reasonable time. The charge will always completely crystallize on cooling; the percentage composition (based on actual data) of the clinker thus obtained would be approximately $3CaO.SiO_2$ 45 per cent., $2CaO.SiO_2$ 35 per cent., and $3CaO.Al_2O_3$ 20 per cent. The melting temperature of the flux necessary for the production of the clinker is materially lowered by the presence of small amounts of impurities; that the small amounts of $Fe_2O_3$, MgO, etc., in commercial cement actually have this effect is shown by the fact that the temperature required for burning is about 1425° C.

In the foregoing discussion we have followed to completion the course of the reactions which take place when cement clinker composed of pure CaO, $Al_2O_3$, and $SiO_2$ is burned; in other words, we have shown the formation of the compounds during the burning of mixtures of these three oxides in the proper proportions for cement clinker, and stated what compounds will be present in the final product if the burning is continued long enough and at a sufficiently high temperature.

The foregoing data, presented in a more concise manner, are given in Table II, which gives the constituents of Portland cement present between rather definite temperature intervals during the burning of this clinker. This table requires no special discussion. It may be well to mention, however, that, while free CaO is present at 1450° C., it will be entirely combined when the temperature reaches 1650° C.

TABLE II.

*Formation of Constituents of Portland Cement During the Burning of the Clinker Composed Only of CaO, $Al_2O_3$, $SiO_2$.*

| Raw mix | 1000° C. | 1000°–1335° | 1335°–1450° | 1450°–1650° | Cool clinker |
|---|---|---|---|---|---|
| CaO (as $CaCO_3$) | CaO | CaO | CaO | CaO | $2CaO.SiO_2$ |
| $Al_2O_3$ | $Al_2O_3$ | $5CaO.3Al_2O_3$ | $3CaO.Al_2O_3$ | $2CaO.SiO_2$ | $3CaO.SiO_2$ |
| $SiO_2$ | $SiO_2$ | $2CaO.SiO_2$ | $2CaO.SiO_2$ | $3CaO.SiO_2$ | $3CaO.Al_2O_3$ |
| | | $3CaO.Al_2O_3$ | $3CaO.SiO_2$ | Flux | |
| | | | Flux | | |

The description and table, showing the essential reactions which take place when cement made up only of CaO, $Al_2O_3$, and $SiO_2$ is burned applies equally well to commercial Portland cement. In commercial cements, however, there are always present small amounts of $Fe_2O_3$, MgO, alkalies, etc. These minor components, which total less than 10 per cent., have but little effect on the major constituents of the clinker. During the burning of cement clinker, however, these minor components play an important part, since their presence insures the formation of a flux at a much lower temperature, and thereby materially promotes the combination of CaO with $Al_2O_3$ and $SiO_2$.

In order to afford a comparison of the chemical compositions, the temperature required for burning, and the final products obtained for different types of Portland cement, the necessary data have been collated in Table III. The examples given in this table are based on the average for a large number of analyses of each of three types of Portland cement, viz., pure cement, made only of CaO, $Al_2O_3$, and $SiO_2$; commercial white cement; and the more common gray variety of Portland cement.

TABLE III.

*Compositions and Burning Temperatures of Various Portland Cements.**

| Portland cements | Percentage composition of clinker — Actual components | | Burning temperature °C. | Constituents of resulting cements | |
|---|---|---|---|---|---|
| Pure (*F*) | CaO 68.4; $Al_2O_3$ 8.0; $SiO_2$ 23.6 | 100.0 | 1650.. | $2CaO.SiO_2$; $3CaO.SiO_2$; $3CaO.Al_2O_3$ | |
| White (*A*) | CaO 66.2; $Al_2O_3$ 6.4; $SiO_2$ 25.0 | 97.6 | 1525.. | $2CaO.SiO_2$; $3CaO.SiO_2$; $3CaO.Al_2O_3$ | Small amount of CaO |
| | MgO, $Fe_2O_3$, $Na_2O$ and $K_2O$ | 2.4 | | | |
| Gray (*B*) | CaO 63.2; $Al_2O_3$ 7.7; $SiO_2$ 22.4 | 93.3 | 1425.. | $3CaO.SiO_2$; $3CaO.SiO_2$; $3CaO.Al_2O_3$ | Small amounts of $CaO.3Al_2O_3$ CaO and ferrites |
| | MgO, $Fe_2O_3$, $Na_2O$, $K_2O$ and $SO_3$ | 6.7 | | | |

* The data given in this table are based largely on the work of this laboratory. The analyses of commercial clinkers are from publications from the Bureau of Standards and from "Portland Cement," by R. K. Meade. The temperatures of burning and the constituents given are based both on our work and that of the Bureau of Standards.

If the raw material for pure cement is perfectly burned at a temperature of 1650°, the clinker obtained will consist of the three compounds — dicalcic silicate, tricalcic silicate, and tricalcic aluminate. The example of a pure cement given in Table III has the chemical composition 68.4 per cent. lime, 8.0 per cent. alumina, and 23.6 per cent. silica. The raw material for white commercial

cement, when burned at a temperature of 1525°, will produce a clinker which consists largely of the same three compounds found in pure clinker, except for a small amount of free lime. The average chemical composition of this type of cement as given in the table is 66.2 per cent. lime, 6.4 per cent. alumina, 25 per cent. silica, and 2.4 per cent. magnesia, iron oxide, and alkali. The clinker obtained on burning the raw material for commercial gray cement at 1425° will consist largely of the same three compounds found in the other two types of clinker, except for small amounts of free lime, the compound $5CaO.3Al_2O_3$, and iron oxide as ferrites. The composition of this clinker is 63.2 per cent. lime, 7.7 per cent. alumina, 22.4 per cent. silica, 6.7 per cent. MgO, $Fe_2O_3$, alkali, and $SO_3$.

The similarity of these three types of cement clinkers is not surprising if we consider their chemical compositions, the content of lime, alumina, and silica of each type being over 90 per cent. We should expect, therefore, and it has been found experimentally to be true, that these three types of cement clinker are made up largely of the same constituents, tricalcic silicate, dicalcic silicate, and tricalcic aluminate, all compounds of the three major components of cement.

Having shown that the components of Portland cement are CaO, $Al_2O_3$, and $SiO_2$, and that the constituent substances are definite compounds of these oxides, let us consider the percentage of these compounds in the clinker. For example, let us take the average gray cement whose chemical composition has been given in Table III. If the clinker for this cement has been perfectly burned, it will consist of about 36 per cent. $3CaO.SiO_2$, 33 per cent. $2CaO.SiO_2$, 21 per cent. $3CaO.Al_2O_3$, and 10 per cent. of the minor constituents.

In the actual manufacture of Portland cement, however, the clinker is not always perfectly burned; that is, the raw materials are not always ground fine enough or heated to a sufficiently high temperature so that the chemical reactions are completed. The proportions of the constituents in commercial cement will then be somewhat different from those given. With our present knowledge of the nature of the chemical reactions, however, it is possible to state which of the constituents will not be completely formed. It will be remembered that, in the discussion of these chemical reactions, it was shown that $3CaO.SiO_2$ is the last constituent to

form completely, and that this compound is formed by combination of CaO with the compound $2CaO.SiO_2$. It is evident, therefore, that when commercial clinker is not perfectly burned there is less $3CaO.SiO_2$ and more $2CaO.SiO_2$,[12] and CaO will be present as an individual constituent. In the example given there will be less than 36 per cent. $3CaO.SiO_2$, more than 33 per cent. $2CaO.SiO_2$, and there will be a certain percentage of free CaO. The exact percentages will, of course, depend upon how near to completion the reaction, $CaO + 2CaO.SiO_2 = 3CaO.SiO_2$, has been carried.

That the manufacture of good Portland cement necessitates that this reaction be carried practically to completion is evident if we consider certain facts in regard to the influence of lime on the physical properties of Portland cement. Practical experience has shown that cements containing much free lime are unsound, and that concrete made from them will in time disintegrate. This is due to the expansion of free or uncombined lime when it reacts with water to form calcium hydrate. If, however, the lime in cements is all combined, they are sound and of good strength. The importance of the reaction $CaO + 2CaO.SiO_2 = 3CaO.SiO_2$ is, therefore, apparent, since this reaction must go practically to completion in order that a sound cement may be produced. It has long been recognized that anything which will promote the combination of lime during burning will promote soundness in cement, and that the greater the percentage of combined lime the greater the strength of the cement.

The average lime content of cement to-day is about 62.5 per cent., which is largely combined as $3CaO.SiO_2$, $2CaO.SiO_2$, and $3CaO.Al_2O_3$. If the percentage of CaO were increased it would tend to combine with the $2CaO.SiO_2$ to form more $3CaO.SiO_2$, and would so combine if the time of burning were long enough and the temperature sufficiently high. Since practical experience has

[12] The "dusting," commonly observed in under-burned clinker when cooled, is due to the 10 per cent. expansion which accompanies the change of $\beta$ $2CaO.SiO_2$ (stable at the clinkering temperature) to $\gamma$ $2CaO.SiO_2$, the crystalline form of dicalcic silicate stable at temperatures below 600° C. This dusting ordinarily takes place only when the clinker contains a very high percentage of $\beta$ $2CaO.SiO_2$, and does not take place when the clinker has been well burned. This $\beta$ form of dicalcic silicate is, however, always present in a considerable quantity in well-burned clinker, so that the dicalcic silicate in cement clinker when cooled is in a state of unstable equilibrium.

shown that increased percentage of lime increases both the percentage of $3CaO.SiO_2$ and the strength of cements, it may be inferred that the strength of cements is largely due to the compound $3CaO.SiO_2$. If this is true, it is desirable that Portland cement should contain as high a percentage of this compound as is possible. An average Portland cement contains about 30 to 35 per cent. of this constituent. That Portland cement contains such a small amount of $3CaO.SiO_2$ is due partly to the fact that this constituent is formed with great difficulty and also to the fact that about 35 per cent. is the maximum yield which could be obtained from raw materials having the same CaO, $Al_2O_3$, and $SiO_2$ composition as is now used.

Before taking up, however, a discussion of the probable value of $3CaO.SiO_2$ as a cementing material and the possibility of increasing its percentage in Portland cement, let us consider what is known as to the cementing value of the constituents of Portland cement, taking up first the changes which take place when Portland cement is mixed with water and hardens.

When Portland cement is finely pulverized and mixed with water, a hard mass is formed by chemical action between the water and the constituents of the cement. The first change undergone by the cement mortar in passing from a plastic to a solid state is called "setting," which requires not over a few hours. After the mortar has set there is a gradual increase in the strength of the mass, and the cement is said to "harden." It sometimes requires a year's time for a cement to acquire its full strength.

While there is still much to be learned as to the chemistry of the hardening of Portland cement, sufficient data on the hydration of the individual major constituents have been obtained to enable us to account for this gradual hardening and increase in strength and to indicate the relative value of these constituents as cementing materials.

Let us now consider the hydration of the three major constituents, $3CaO.Al_2O_3$, $3CaO.SiO_2$, and $2CaO.SiO_2$, in the order named. When pure $3CaO.Al_2O_3$ is mixed with water an amorphous hydrated material is first formed. This material sets and hardens very rapidly. The compound $3CaO.SiO_2$, when mixed with water, also sets and hardens rather rapidly. In the case of this compound, as in the case for $3CaO.Al_2O_3$, the setting and hardening are due to the formation of an amorphous hydrated

material on the individual grains, which are thus cemented together. The extent of the hydration or the percentage of amorphous material which each grain will yield depends upon the percentage of water used and the time. With a given percentage of water the amount of amorphous material formed from the compound $3CaO.Al_2O_3$ in a given time is much greater than for the compound $3CaO.SiO_2$; that is, the compound $3CaO.Al_2O_3$ reacts with water much more rapidly than the $3CaO.SiO_2$. The compound $2CaO.SiO_2$ reacts very slowly with water, and it is only after a long period of time that sufficient amorphous hydrated material is formed to cement together the grains of this compound and so form a hard mass.

The amorphous hydrated material formed by the action of water on the constituents of cement does in time, no doubt, crystallize to some extent. From the data available it would appear that the crystals formed are calcium hydrate and some crystalline hydrate derived from $3CaO.Al_2O_3$. Apparently no crystalline hydrate of the calcium silicates is formed.

From this brief description of the action of water on the constituents of Portland cement it will be seen that the setting and hardening of Portland cement involve the formation of an amorphous hydrated material which subsequently partially crystallizes; that the initial set is probably due to the hydration of $3CaO.Al_2O_3$; that the hardness and cohesive strength at first are due to the cementing action of the amorphous material produced by the hydration of this aluminate and of the $3CaO.SiO_2$; and that the gradual increase in strength is due to further hydration of these two compounds, together with the hydration of the $2CaO.SiO_2$.

Of the three compounds which thus take part in the setting and hardening of Portland cement, the $3CaO.SiO_2$ appears the best cementing constituent; that is, this compound is the only one of the three which when mixed with water will set and harden within a reasonable time to form a mass which in hardness and strength is comparable to Portland cement. The compound $2CaO.SiO_2$ requires too long a time to set and harden in order to be in itself a valuable cementing material. The compound $3CaO.Al_2O_3$, while it sets and hardens rapidly, is rather soluble in water and is not particularly durable or strong.

From this it would appear that the compound tricalcic silicate

is *the* essential constituent of Portland cement; consequently the higher its percentage the better the cement. Before discussing the nature of an investigation which might lead to the production of a cement containing a high percentage of this compound, however, let us briefly reconsider the theories of Vicat in order to show the similarity between what appears to have been the ideal cement of his mind and tricalcic silicate.

Vicat, it will be remembered, seemed to believe that the lime in cement mortar should be in a state of chemical combination, and that it were best that it should be so combined with gelatinous silica.

When tricalcic silicate is mixed with water to form a mortar a gelatinous material is formed which is composed of hydrous lime and silica. Whether the lime and silica continue to be chemically combined or whether the gelatinous material is colloidal is still a matter of some uncertainty, although it would appear that this material is colloidal.

The similarity between Vicat's theoretical cement and tricalcic silicate is thus apparent.

The basis for Vicat's theoretical reasoning was undoubtedly derived from his observations on the action of hydrated lime when ground with water and pozzolana, a material which contains over 40 per cent. silica, with smaller percentages of $Al_2O_3$, MgO, $Fe_2O_3$, and alkalies. This mixture, commonly known as Roman cement mortar, it would now appear, sets and hardens in much the same manner as tricalcic silicate; in the case of Roman cement the formation of the gelatinous material, which subsequently hardens, being due to the action of lime water on the pozzolana. This action, however, is exceedingly slow, and it requires a much longer time for the completion of the hardening in Roman cement mortar than in mortar containing tricalcic silicate. This is undoubtedly due to the nature of the chemical combinations of silica in pozzolana, which react with water much less readily to form gelatinous silica than is the case of the silica combined in tricalcic silicate. This circumstance, that gelatinous silica is released with such readiness when tricalcic silicate is mixed with water, is probably the reason why this compound is such a valuable cementing material. Without discussing at length the nature of the cementing value of gelatinous silica, it may be well to state that it seems probable that certain of the toughest sandstones

(ideal concrete structures) are made up of grains of sand originally cemented together with gelatinous silica which was gradually deposited from solution on to the grains of sand and subsequently hardened.

This foregoing discussion, which tends to prove that gelatinous silica is the most essential constituent of a cement mortar, is somewhat speculative. That such speculation is desirable is due to the fact that by formulating advance theories as to the probable outcome of an investigation one may sooner attain the end. It is essential, however, that theory and established fact be not confused.

With this in mind, let us now consider certain possibilities which might increase the percentage of gelatinous silica in cement mortars. We know at the start in such an investigation that tricalcic silicate is probably the only compound containing silica in combination in such a manner that it is *readily* released to form a thin coating of gelatinous silica when mixed with water to form a mortar. Therefore, until some other compound is discovered in which the silica is combined in such a way that it is more readily available in the gelatinous state, the best way to increase its percentage in cement mortars is to increase the percentage of tricalcic silicate in cement clinker. Unfortunately this is difficult, although there are several very interesting possibilities.

Pure tricalcic silicate is formed by combination of lime and silica only with the greatest difficulty, the temperature of burning required, 1700° C., being too high for industrial practice. In order that this compound form readily and at a sufficiently low temperature so as to become a commercial possibility, it is necessary that some substance or substances other than lime and silica be present during the burning; these substances to be of such a nature that a low-melting, rather fluid flux is formed, so as to facilitate the combination of lime and silica to form tricalcic silicate. At present this flux is to a large extent furnished by the low-melting calcium aluminates in the clinker.

In the discussion of the constitution of Portland cement we have shown that an average Portland cement contains about 30 to 35 per cent. tricalcic silicate, a proportion which closely approaches the maximum possible yield with the present percentage of flux; in other words, if the components are in the proportions of an average Portland cement. It has also been shown that an

increase in the lime content of an average cement will increase the percentage of $3CaO.SiO_2$ if the conditions of burning are such that the reaction $CaO + 2CaO.SiO_2 = 3CaO.SiO_2$ goes to completion. This, however, necessitates finer grinding of the raw materials, as well as burning for a longer time and at an increased temperature, factors which materially affect the cost of production. Now the data discussed above were obtained by applying the results obtained by an investigation of the equilibrium relations found to exist in the system $CaO - Al_2O_3 - SiO_2$ to the actual manufacture of Portland cement; but this by no means implies that in presence of other components the conditions required for the production of an adequate amount of flux should not be more favorable and economical. In other words, the study of other systems may establish the economic possibility of producing a cement containing a high percentage of tricalcic silicate. For example, if some substance were substituted for the component $Al_2O_3$ in the system $CaO - Al_2O_3 - SiO_2$, the study of the equilibrium relations found to exist in this new system would enable one to determine whether or not it would be economically possible to produce a cement containing a high percentage of $3CaO.SiO_2$ from raw materials of which the components are CaO, $SiO_2$, and this third substance. Thus if $Fe_2O_3$ were substituted for $Al_2O_3$, we could, from the study of the system $CaO - Fe_2O_3 - SiO_2$, ascertain the fineness of the raw material and the time and temperature of burning necessary to secure a clinker containing the highest percentage of $3CaO.SiO_2$ which could be economically produced from raw materials of which the major components are CaO, $Fe_2O_3$, and $SiO_2$. This would require that one determine the nature of all compounds formed in mixtures of these three oxides which when burned contain $3CaO.SiO_2$, and that we establish the identity, melting temperature, and rate of formation of $3CaO.SiO_2$ in such mixtures. Instead of substituting a single substance, it would undoubtedly be more desirable to substitute a number of different substances, since the presence of several produces a lower melting flux and thus makes possible the formation of $3CaO.SiO_2$ at a lower temperature. By proceeding in this way to determine systematically the various mixtures of substances which when burned give high percentages of $3CaO.SiO_2$, it would not seem at all improbable that we may discover some mixture which could be economically manufactured and which would

result in the production of a cement far superior to the Portland cement now made.

In conclusion, let us recapitulate the main points contained in this paper. The value of Portland cement depends upon the fact that when finely powdered and mixed with water it forms a hard mass; and the strength and permanence of this mass depend upon the constituents of the cement. The major constituents are tricalcic silicate, dicalcic silicate, and tricalcic aluminate. Of these constituents, the compound tricalcic silicate is the one which hardens and develops the greatest strength within a reasonable time. This most important constituent, which is the one formed with the greatest difficulty, makes up only about 30 to 35 per cent. of an average normal Portland cement. It may be said, therefore, that the essential process for the manufacture of Portland cement is the formation of this compound, and that any improvement in this process yielding an increased percentage of tricalcic silicate will increase the cementing value of Portland cement. In order to determine the most economical process for producing tricalcic silicate in the highest percentages, it will be necessary to study the rate of formation of this compound in a series of mixtures of various substances; this, in turn, necessitates the determination of the equilibrium relations of tricalcic silicate at high temperatures in such mixtures. Such a procedure will lead sooner to the discovery of the optimum composition in various cases and for various purposes than the empirical, cut-and-try methods which hitherto have been the only methods tried.

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D. C., March 2, 1916.

# THE RULING AND PERFORMANCE OF A TEN-INCH DIFFRACTION GRATING.*

BY

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THE principal element in the efficiency of any spectroscopic appliance is its resolving power—that is, the power to separate spectral lines. The limit of resolution is the ratio of the smallest difference of wave-length just discernible to the mean wave-length of the pair or group. If a prism can just separate or resolve the double yellow line of sodium its limit of resolution will be $\frac{5896-5890}{5893}$, or approximately one one-thousandth, and the resolving power is called one thousand.

Until Fraunhofer (1821) showed that light could be analyzed into its constituent colors by diffraction gratings this analysis was effected by prisms the resolving power of which has been gradually increased to about thirty thousand. This limit was equalled, if not surpassed, by the excellent gratings of Rutherford, of New York, ruled by a diamond point on speculum metal, with something like 20,000 lines, with spacing of 500 to 1000 lines to the millimetre. These were superseded by the superb gratings of Rowland with something over 100,000 lines, and with a resolving power of 150,000.[1]

The theoretical resolving power of a grating is given as was first shown by Lord Rayleigh by the formula $R = mn$, in which $n$ is the total number of lines, and $m$ the order of the spectrum.

An equivalent expression is furnished by $R = \frac{l}{\lambda}(\sin i + \sin \theta)$, where $l$ is the total length of the ruled surface, $\lambda$ the wave-length of the light, $i$ the angle of incidence, and $\theta$ the angle of diffraction, and the maximum resolving power which a grating can have is that corresponding to $i$ and $\theta$, each equal to 90°, which gives $R = \frac{2l}{\lambda}$ that is, twice the number of light-waves in the entire length of the ruled surface.

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* Presented at the stated meeting held Wednesday, November 17, 1915.

[1] The 6½-inch gratings now ruled on the Rowland engine have a much higher resolving power—probably 400,000.

This shows that neither the closeness of the rulings nor the total number determines this theoretical limit, and emphasizes the importance of a large ruled space.

This theoretical limit can be reached, however, only on the condition of an extraordinary degree of accuracy in the spacing of the lines. Several methods for securing this degree of accuracy have been attempted, but none has proved as effective as the screw. This must be of uniform pitch throughout, and the periodic errors must be extremely small.

For a short screw—for example, one sufficient for a grating two inches in length—the problem is not very difficult, but as the length of the screw increases the difficulty increases in much more rapid proportion. It was solved by Rowland in something over two years.

Since this time many problems have arisen which demand a higher resolving power than even these gratings could furnish. Among these is the resolution of doubles and groups of lines whose complexity was unsuspected until revealed by the interferometer and amply verified by subsequent observations by the echelon and other methods.

Others that may be mentioned in this connection are the study of the distribution of intensities within the spectral "lines"; their broadening and displacement with temperature and pressure; the effect of magnetic and electric fields, and the measurement of motions in the line of sight, as revealed by corresponding displacement of the spectral lines in consequence of the Doppler effect.

All of these have been attacked with considerable success by observations with the echelon, the interferometer, and the plane-parallel plate. These methods have a very high resolving power, but labor under the serious disadvantage that adjacent succeeding spectra overlap, making it difficult to interpret the results with certainty.

Some twelve years ago the construction of a ruling engine was undertaken with the hope of ruling gratings of fourteen inches —for which a screw of something over twenty inches is necessary. This screw was cut in a specially corrected lathe so that the original errors were not very large, and these were reduced by long attrition with very fine material until it was judged that the

residual errors were sufficiently small to be automatically corrected during the process of ruling.

The principal claim to novelty of treatment of the problem lies in the application of the interference method to the measurement and correction of these residual errors.

For this purpose one of the interferometer mirrors is fixed to the grating carriage, while a standard, consisting of two mirrors at a fixed distance apart, is attached to an auxiliary carriage. When the adjustment is correct for the front surface of the standard, interference fringes appear. The grating carriage is now moved through the length of the standard (one-tenth of a millimetre if the periodic error is to be investigated; ten or more millimetres if the error of run is to be determined), when the interference fringes appear on the rear surface. This operation is repeated, the difference from exact coincidence of the central (achromatic) fringe with a fiducial mark being measured at each step in tenths of a fringe (twentieths of a light-wave). As a whole fringe corresponds to one hundred-thousandth of an inch, the measurement is correct to within a millionth of an inch.

The corresponding correction for periodic errors is transferred to the worm-wheel which turns the screw; and for errors of run to the nut which moves the carriage.

In this way the final errors have been almost completely eliminated and the resulting gratings have very nearly realized their theoretical efficiency.

A number of minor points may be mentioned which have contributed to the success of the undertaking.

(*a*) The ways which guide the grating carriage, as well as those which control the motion of the ruling diamond, must be very true; and these were straightened by application of an autocollimating device which made the deviation from a straight line less than a second of arc.

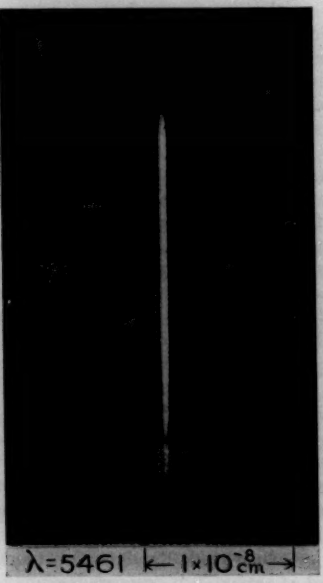
(*b*) The friction of the grating carriage on the ways was diminished to about one-tenth of that due to the weight (which may amount to twenty to forty pounds) by floating on mercury.

(*c*) The longitudinal motion of the screw was prevented by allowing its spherically rounded end to rest against an optically plane surface of diamond which could be adjusted normal to the axis of the screw.

(*d*) The screw was turned by a worm-wheel (instead of pawl and *ratchet*) which permits a simple and effective correction of the periodic errors of the screw throughout its whole length.

(*e*) A correcting device which eliminates periodic errors of higher orders.

(*f*) It may be added that the nut which actuates the carriage




Enlargement of photograph of the green mercury line $\gamma$ 5461, taken by H. L. Lemon with ten-inch diffraction grating in sixth order. Ruled surface, 9¼ inches × 2¼ inches, 11,700 lines per inch. Mounted in Littrow form with eight-inch lens by Brashear. Focal length 20 feet.

had bearing surfaces of soft metal (tin) instead of wood, as in preceding machines. It was not found necessary to unclamp the nut in bringing it back to the starting point.

Finally it may be noted that instead of attempting to eliminate the errors of the screw by long-continued grinding—which in-

evitably leads to a rounding of the threads—it has been the main object to make these errors conveniently small; but especially to make them constant—for on this constancy depends the possibility of automatic correction.

The accompanying photograph made with a ten-inch grating, sixth order (actual ruled surface 9.4 inches by 2.8 inches), used in the Littrow form with an excellent eight-inch lens by Brashear, is given in evidence of its performance. The resolving power as shown by the accompanying scale of Angström units is about 450,000. The original negative shows a resolving power of about 600,000. The theoretical value is 660,000.

Doubtless the possibility of ruling a perfect grating by means of the light-waves of a homogeneous source has occurred to many —and indeed this was one of the methods first attempted.

It may still prove entirely feasible—and is still held in reserve if serious difficulty is encountered in an attempt now in progress to produce gratings of twenty inches or more. Such a method may be made partly or perhaps completely automatic, and would be independent of screws or other instrumental appliances.

It may be pointed out that an even simpler and more direct application of light-waves from a homogeneous source is theoretically possible and perhaps experimentally realizable.

If a point source of such radiation sends its light-waves to a collimating lens and the resulting plane waves are reflected at normal incidence from a plane surface, stationary waves will be set up as in the Lippman plates; these will impress an inclined photographic plate with parallel lines as in the experiment of Wiener; and the only limit to the resolving power of the resulting grating is that which depends on the degree of homogeneity of the light used. As some of the constituents of the radiations of mercury have been shown to be capable of interfering with difference of path of over a million waves, such a grating would have a resolving power exceeding a million.

This investigation has had assistance from the Bache Fund of the National Academy of Science, from the Carnegie Institution, and from the University of Chicago.

In addition to the grateful acknowledgment to these institutions, I would add my high appreciation of the faithful services rendered by Messrs. Julius Pearson and Fred Pearson.

**Electrically-driven Rolling-mill Service by a Central Station.** ANON. (*Electrical World*, vol. 67, No. 12, March 18, 1916.)—The objections which many central-station companies raise to rolling-mill loads (extreme fluctuations and consequent disturbing effect on line voltage) have been overcome, to a great extent, in the plant of the Central Steel Company, of Massillon, Ohio, by supplying energy to the main motor of its large blooming mill through a fly-wheel induction motor-generator, regulating the slip of the latter, and so exciting the motor-generator and blooming-mill motor that peak energy is absorbed from the rotating fly-wheel, minimizing the disturbances to the electric system. Another feature of the installation is that the blooming-mill reversing motor is connected permanently with the generator terminals without any control apparatus in series, the speed being regulated within the range of 0–r. p. m. to 47–r. p. m. by changing the generator field excitation. The generator and reversing motor are separately excited from a motor-driven exciter set employed especially for this equipment, so that operation is dependent only on continuity of the alternating-current supply and not on the excitation system common to all equipment in the mill.

When an ingot approaches the blooming mill the motor is turned over slowly until the rolls grip the metal, then the speed is increased to 47–r. p. m. to complete the roughing passes. During the finishing passes the motor speed is still further increased by weakening the motor field. Racing cannot occur when the motor is turning over idly before the metal enters the rolls, since the speed is practically independent of the load. This is a distinct advantage over operation with steam engines, since they usually race when operated without load, or come to a standstill when the rolls grip the metal.

At the end of each pass the generator field is de-energized and the mill motor brought to rest by regeneration. During this period it "pumps" energy back into the fly-wheel generator set, thereby speeding it up preparatory to the gripping of the metal in the next pass. Approximately 70 per cent. of the energy required to accelerate the rotating parts of the mill is regained in this manner. Reversal of the blooming-mill motor is accomplished by reversing the direction of the shunt-field current, through the generator, residual magnetism being killed by automatically-actuated, field-forcing relays. In this operation accelerating relays increase the motor torque by cutting in resistance to decrease the field current of the main motor, thereby increasing the current through the motor armature.

Although the reversing motor develops peaks of 8100 horsepower, the input to the alternating-current motor does not exceed 1200 kilowatts. In other words, the central station's generating equipment need not exceed the rating required to generate 1200 kilowatts. Furthermore, the steam economies obtained under such conditions are considerably better than those obtained from operating a reversing engine directly from a boiler plant. At this plant from 20 kilowatt-hours to 30 kilowatt-hours is sufficient for rolling different grades of metal, including vanadium steels.

# HIGHWAY PROBLEMS OF THE STATE OF PENNSYLVANIA.*

BY

WILLIAM D. UHLER,

Chief Engineer, Pennsylvania State Highway Department.

THE commonwealth of Pennsylvania comprises more than 44,000 square miles of territory. The total road mileage in the state is 97,850, or more than two miles of roadway to each square mile of land. This mileage would have been more than sufficient to have laid out this vast territory along sectional lines, as has been done in some of the western states, which procedure would have simplified the highway problems for the commonwealth.

The earliest settlements in the state were in the extreme southeastern portion, centring in and about this historic City of Brotherly Love, where William Penn brought the voyagers on the staunch little ship *Welcome* to found his colony as "a religious experiment."

Even before the autumn of 1628, when the *Welcome* arrived, the upper end of the Delaware Peninsula had been settled by the hardy Swedes, and even then the Indians who roamed the old Welsh tract knew the sight of the palefaces.

With Philadelphia established by Penn and his adherents, the growth of Pennsylvania began. Of necessity these early settlers established their system of roads and lanes which later became the city streets. Within five years the more adventurous in the colony had crossed the Schuylkill and pushed into the virgin land to the west and north, and in 1687 the first main highway leading westward from Philadelphia was formally laid out. It was known as the French Creek Road and followed the western bank of the Schuylkill River to the confluence with French Creek, which point later became the site of the present Phœnixville, thence following French Creek to the westward. The highway was opened to a point near the Conestoga Creek, or River, and within a few years was further completed through the town of Lancaster.

* Presented at a meeting of the Mechanical and Engineering Section held Thursday, February 24, 1916.

One of the earliest notes made concerning highways in the province was on September 19, 1686, when the attention of Councill was called to " ye unevenesse of ye Road from Philad^a. to ye falls of Delaware." This was the King's Highway. Another mention in the records is on June 27, 1693, of the main highway between the Swede settlement on the Delaware and the Dutch settlement on the Hudson which, in this later day, we know as the Old York Road. This was laid out over 77 courses, 9610 perches, or 30 miles, and was confirmed January 7, 1713.

So rapidly did the hardy young colony increase in population, through immigration, that the early days of the eighteenth century

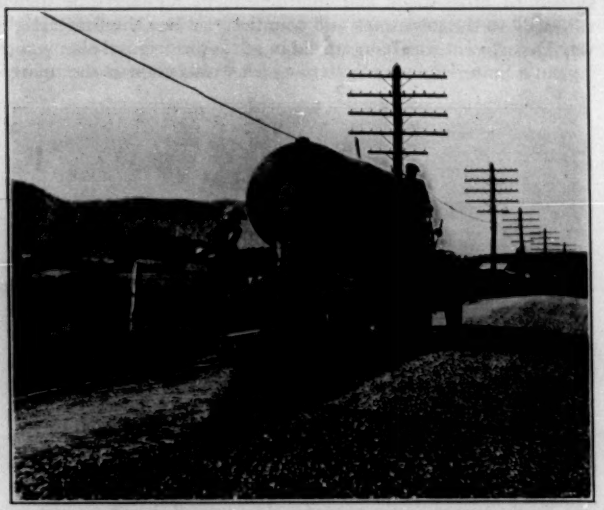
Culvert on state highway after improvement.

saw Pennsylvania, east of the Susquehanna River, well in process of permanent settlement. In fact, in those colonial days, when the site of this historic building was well out in suburban Philadelphia, the state of Pennsylvania had acquired through its settlements a road mileage of no mean proportions.

These roughly-made roads, or trails, radiating in different directions from Philadelphia through the southeastern part of the state, were the parent branches from which spread and grew an intricate and complicated system of cross-lanes and by-ways now forming a part of the vast road mileage of the state.

As was the case in nearly every instance in colonial America, the roads laid out followed the general direction of one of three

classes of trails: the Indian trail, animal paths, or waterway courses. For a few years the French Creek Road answered the requirements for traffic to the west from Philadelphia, although in the same year that it was opened a road was laid down from the western banks of the Schuylkill River to Old Haverford Meeting House, and in 1690 this highway was pushed still farther



Modern method of applying bituminous surface treatment.

westward, forming the beginning of the famous old Conestoga Road. In 1693 and 1695 this road was extended westward to the Susquehanna. The main line of the Pennsylvania Railroad, from Philadelphia to Lancaster, follows closely the original lines of this highway, although our historic records are misty in their references to its exact location after entering that part of the parent county of Chester which constitutes that county as we now know it. There seems to be basis for the belief that the Conestoga Road originally passed through the village of Goshen, now known as West Chester.

In 1701 a third highway was projected westward from Philadelphia, referred to in the chronicles of the times as the Nottingham and New Kensington Road. Later this highway was continued through the colony of Maryland to Baltimore and became known as the Baltimore Pike.

From these primary arteries, as has been said before, grew the system of cross-roads and interdependent highways belonging variously to the townships and counties. When the State Highway Department was reorganized in 1911, the original plan was to lay out a State Highway System which would connect the county-

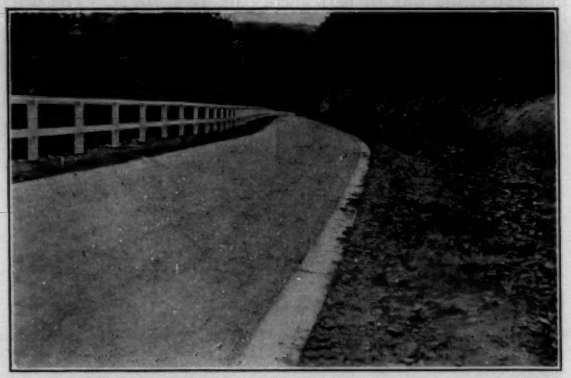
Effect of motor traffic on plain water-bound macadam.

seats in the state by means of the most-travelled and most direct roads. This laudable intention was frustrated, in a measure, by the desire of various communities to have greater mileage in their localities added to this State Highway System; the net result being that the Sproul Act, under which the State Highway System was designated, provided for 8800 miles being taken over by the commonwealth. This was far too much. Nothwithstanding this fact, the Legislature of 1913 added more than 1400 miles to the system. Had it not been for the firm stand taken by Governor Brumbaugh, the 1915 Legislature would have continued to increase this mileage by adding other routes to the Sproul system.

This vast mileage falls on the state to maintain and reconstruct.

From the viewpoint of highway efficiency, the system, as constituted, makes for Pennsylvania's greatest mistake. No other state in the Union has attempted the control of so great a road mileage. Rather, the practice has been to take over those highways which have been reconstructed with a permanent type of road material and to assume no responsibility for their maintenance prior to that time.

Far better would it have been for Pennsylvania had a main line system of roadways been adopted directly connecting the county-seats and following the main courses of travel east and



Improved state highway, showing bituminous concrete wearing surface.

west and north and south. This would have meant a State Highway System not exceeding 3300 miles, which would have been feasible and comparatively easy to maintain with the revenues at the disposal of the commonwealth for highway purposes.

At the present time the department is working up such a comprehensive plan of main arteries. It is proposed to secure, if possible, the approval of Governor Brumbaugh to this plan, in which event all permanent improvements in the future will be limited to this main system until it is completed, after which the laterals will be improved from time to time as appropriations become available.

In taking over and assuming the responsibility of 10,200 miles

comprising the system, only a small percentage of which was improved, the state shouldered a burden too great to be carried in a proper manner. To demonstrate the wisdom of the policy adopted in other states, I would call your attention to the fact that the Pennsylvania State Highway Department during 1915 spent approximately four and one-half million dollars in maintaining the present system of 10,200 miles, and, from present indications, will spend during the year 1916 for the same purpose approximately three million dollars, making a total expenditure of seven and one-half million dollars in two years, with nothing of any great moment in the way of permanency to show for it. The work

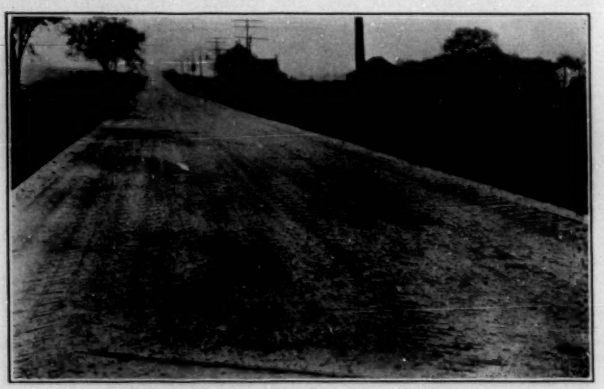
Bituminous surface-treated state highway.

done during 1915 was the maintenance of 6648 miles of earth, flint, gravel, and shale roads; resurfacing 525 miles of water-bound macadam roads; oiling 1084 miles of roads, and maintaining 1355 miles of stone and other improved roads. These figures show conclusively that the method under which we are working is by far the most expensive way to build up a road system.

Had it been possible to expend this seven and one-half million dollars in permanent construction, from five to six hundred miles of highways could have been improved during the working seasons of 1915 and 1916, which, added to the 1880 miles of roads

already improved, would have furnished a satisfactory nucleus for the permanent highway system of the state.

I might add that it is the policy of this administration to maintain the present road mileage before attempting any new construction work. We have a large mileage of old state-aid roads, together with toll roads taken over, which require resurfacing in order to save what little is left of the original improvement, so that, as before stated, the work done during the seasons of 1915 and 1916 primarily has been and will be that of maintenance. The general practice in handling the various types of roads is as fol-



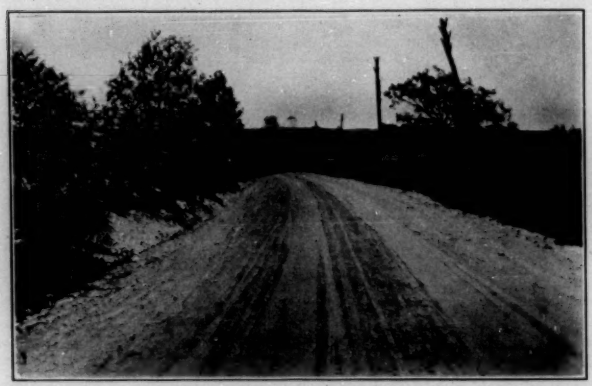
Effect of traction engine traffic on improved highway.

lows: earth roads, to provide proper drainage and shape by use of road machines and to preserve the shape and contour by the liberal use of log drags; water-bound macadam roads, to resurface and patch where necessary and then to preserve this surface by the use of a bituminous surface treatment; brick, asphalt, concrete, etc., to make such repairs as may be necessary to keep the road in good condition.

After all improved surfaced roads have been repaired they are taken care of under the patrol system which has been inaugurated in the department. This provides for the placing of caretakers or patrolmen in charge of sections of highway from three to five miles in length, depending upon the character of the road to be

maintained. Each patrolman is provided with such tools, material, and equipment to take care of his section of road properly. This method has been found to be not only more satisfactory but also more economical than any other devised for the maintenance of highways.

There is no doubt but that the problems of the Pennsylvania Highway Department have been greatly complicated by the character of the roads unloaded, as it were, upon the state. In a number of cases roads which had been neglected for years and, in some instances, abandoned roads, were deliberately bequeathed



Earth road maintained with log drags.

to the state. As an illustration of this, let me cite one section where five routes, leading north from one of the east and west main highways, were laid down within a distance of 20 miles. One route, 24 miles in length, is not open to traffic at the present time, as a portion of it runs over what is left of the right of way of an abandoned narrow-gauge railroad, the graded road-bed of which, for a greater portion of the distance, is not more than five feet in width. The rest of the location of this state highway follows old lumber trails which it would be necessary to re-locate and grade.

The second route runs along the Susquehanna River. It should be, and undoubtedly was, a very important thoroughfare

to the northwest, but, when the railroad was built along the river, the right of way of the highway disappeared. To put a road of sufficient width in this location at the present time would require either the construction of a retaining wall along the river nearly the entire length of the road, or heavy grading to place the highway between the railroad and the mountain side, as high bluffs are encountered along the whole line. In either event this would mean an expenditure of at least twenty or thirty thousand dollars a mile, exclusive of road surfacing.

The third state highway, in the locality to which I refer, is an historic one which virtually has been abandoned by the local authorities for the past generation. The right of way is covered with underbrush, and but little remains to indicate that it once was a prosperous and much-travelled highway to the frontier.

Of the fourth state highway, running off from this east and west trunk line, only a short distance is safe for traffic. The railroad built through here forced the re-location of this highway. In many places it was thrown up on the side hill to permit the railroad company the use of the original location. At several points the road now is not more than 8 or 9 feet in width, with almost precipitous slopes.

The fifth of these highways is the only one that can be put in passable condition at a small expense.

These examples simply serve to illustrate one of the many problems confronting the Department. Of these five roads only one would be used in a main system of highways.

The toll road is another problem to be considered. At the time the Sproul Act was passed there were 717 miles of toll roads in Pennsylvania, of which 521 miles were taken into the State Highway System. Since that time 105 miles of these roads have been acquired by the State Highway Department through purchase, leaving 416 miles still on state highway routes, the major portion of them being in thickly-populated and heavily-travelled sections of the state. The toll roads, as originally built, were of great benefit in the early development of the state, but to-day one looks upon them as a relic of the Dark Ages. They are an anachronism! Nevertheless, this subject is one that must be reckoned with, and the expenditure of large sums will be necessary before all the toll roads are acquired finally by the state.

We should not lose sight of the fact that the improvement of

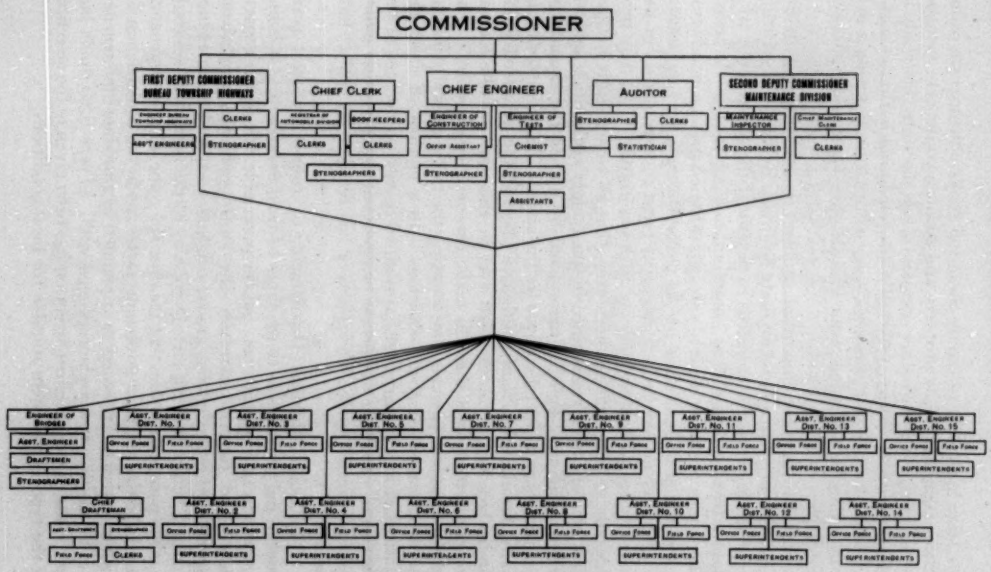
PENNA STATE HIGHWAY DEPT.
ROAD MAP
OF
PENNSYLVANIA
showing
STATE HIGHWAYS
as adopted by the Legislature in 1911 and approved
May 31, 1911, and subsequent amendments
LEGEND
Stone or gravel road
Earth road improved
Earth road
Trail
STATE HIGHWAYS AND BRIDGES TO JANUARY 1, 1914.
Total State Highways constructed 1904 to 1913 inclusive 1,884.19
Stone or gravel road (Surface Treated) 1,251.19
Earth Roads Improved 282 632.44
Improved Roads Maintained 265 634.65
Earth Roads Maintained 283 53.00
Roads Abandoned 283 .904.42

our state highways adjoining these toll roads enhances the value of this form of private property and means a consequent increase in the price which the owners demand when the state gets ready to take them over. Most of the toll roads remaining in Pennsylvania are located in the southeastern corner of the state, forming a network of highways in and about Philadelphia, Lancaster, Lebanon, and York.

By far the most important problem in connection with the development of an up-to-date State Highway System is in securing or providing revenues sufficient to permit of the construction of a main arterial system such as I have outlined previously. Whether such funds are to be derived through taxation or by a bond issue is a question to be decided by the public through the Legislature.

Another problem which causes us great concern is that of the maintenance of bridges on state highway routes. The law provides, or at least so it is interpreted, that all county-built bridges on routes are to be maintained by the county authorities, and all bridges originally built or maintained by and at the expense of townships are to be taken over by the state. This means that in many instances the county authorities neglect the maintenance of the bridges on the routes taken over by the state and the state is powerless to compel them to make the necessary repairs. The travelling public, however, not knowing the facts, naturally blames the department for such conditions. In a number of cases the State Highway Department has notified county authorities of the dangerous condition of certain bridges, but has been met either with a refusal to make the repairs or has received no reply whatsoever.

The State Highway Department, of course, has the usual trouble and problems as to the types of road to be built. It is impossible to satisfy every one, but the invariable rule of the department is to consider carefully the local needs and conditions, together with the traffic, grade, original cost, and maintenance charges, before making any decision as to the type to be selected. It is my personal opinion that the time has come when maintenance should be the principal governing factor, as in the construction of such a system of highways as is planned by this state maintenance will be the first item to be reckoned with. There is no doubt but that in the past insufficient attention has been given to the selection of the type of pavement suitable for local conditions.




Organization of Pennsylvania State Highway Department under Act of 1911. 1916.

Allowance must and should be made in the selection of the type of pavement for a constant increase and change in the character of the traffic. The type that made France famous for its good roads, water-bound macadam, as originally constructed and maintained, will not meet the present-day traffic demands of the motor vehicles.

Since the advent of motor vehicles still further demands are made by the constantly-increasing size and weight of motor trucks now being used, which creates an entirely new condition. There is no question but that either steps will have to be taken in the near future to control this class of traffic or else additional revenues must be raised to permit of more permanent types of construction, as the roads built in the past, in the majority of cases, are neither of sufficient width to permit the safe operation at high speed of the trucks as now constructed with bodies practically the size of freight cars, nor are the foundations sufficient to carry these excessive loads.

The state at the present time derives no revenues from this class of vehicles other than the regular motor license fees of from five to twenty-five dollars a year, depending upon the size of the truck. This is another question that must be settled by the public through its legislative body.

The question of experienced help, including engineers, superintendents, foremen, and even laborers, is a problem confronting us at every turn. We have found it impossible to get sufficient skilled assistants, for the reason that road work, along modern lines, is in its infancy. It is necessary to educate the forces, and one of the chief troubles in holding together the necessary road organization is that it is impossible—in fact, impracticable—to provide work for them during the full twelve months of the year. This is because the character of the work will not permit of continuous employment, and it becomes necessary, usually, to lay off approximately 75 per cent. of the force at the close of the working season. This means that the skilled assistants and good laborers look for work of a more permanent character. Again, in certain parts of the state we have found it impossible to secure any kind of labor and this, of necessity, makes necessary the importation of foreign labor, with all of its drawbacks.

In conclusion, aside from the actual building and maintaining of roads, still another and a very vital question is the proper ad-

ministration of the affairs of the department. Too often has it been the case in public office in this country that political preferment has been exercised to so great an extent that efficiency has been impaired.

In appointing Commissioner Cunningham, Governor Brumbaugh gave him to understand fully that he expected a businesslike administration of the State Highway Department; efficiency is the first consideration. Removals, promotions, and appointments, in both the Engineering and Executive Divisions, have been made solely upon merit. The result is that to-day Pennsylvania has an efficient and economically-operated Highway Department.

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**Water Power and Defence.** W. R. WHITNEY. (*Proceedings of the American Institute of Electrical Engineers,* April 26, 1916.)—The United States has no adequate source of fixed nitrogen. Nitric acid is an absolute necessity in the manufacture of any form of explosive stuffs. Ammonia or nitrate compounds are in increasing demand as fertilizers. The present dependence upon Chile is a menace in case of war and involves the payment of export duties and profits amounting to nearly $5,000,000 annually in time of peace. Home production is wholly a question of initiative and proper utilization of water power. Failure to establish the industry in the past has been due to economic conditions, such as the relative proximity of Chile and the impossibility of competing with the cheap water powers of Scandinavia as well as lack of a near-by agricultural demand. The growing need for fertilizers, the desirability of establishing a dyestuff industry, and, especially, the feeling of uncertainty in international relations make a reconsideration desirable.

National safety demands the development of a nitrogen fixation industry, whether it be self-supporting or not. But, the industry once established, the products would be of the greatest value in times of peace and would be stimulated thereby. Thorough industrial organization is the best preparedness for either peace or war. Each of the processes available has advantages. The problem is many-sided and far-reaching, and hence it is very desirable that the various government departments concerned, those of the Army, Navy, Agriculture, and Interior, with their skilled staffs and expert knowledge, should coöperate in determining the course to be taken. Immediate action is very important, since at least two years will be consumed in getting any process available into operation after a decision is reached.

# THE PRODUCTION OF LIGHT BY ANIMALS.*

BY

ULRIC DAHLGREN,

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## THE LUMINOUS CRUSTACEANS.

A large number of crustaceans are known to light, particularly some numerous forms that live for the most part in very deep water. Practically all of the luminous species are pelagic or bathymic in their habit, and we find some quite simple sorts of light-organs as well as some of the most highly differentiated and organized kinds. As in the cephalopod mollusca, two chief sorts can be distinguished: those that have an external form of combustion and which squirt the luciferine out into the sea-water, and those that have an internal form of combustion (oxidation from the blood) and have their organs furnished with reflectors, lenses, etc. It can also be noticed that the various types of organs have developed quite independently and have no phylogenetic or evolutionary relationship with each other.

We will consider the following groups of organs: 1. Those found on the Ostracod. 2. Those met with among the Copepoda. 3. The light organs possessed by the Schizopod crustacea. 4. The decapod types of light organs.

### *Ostracoda.*

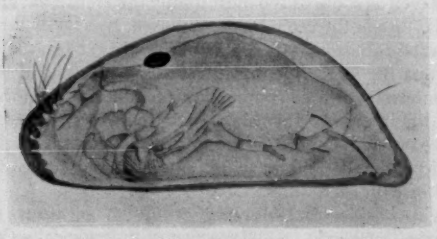
Mangold gives a very complete account of the various works that have been done on the Ostracods (see Fig. 1). Godeheu de Riville first noticed, in 1754, great quantities of these small crustaceans in the waters of Malabar giving out a sky-blue light. Müller mentions this and further tells of a number of species of this group that showed light, as *Pyrocypris chierchiæ, Pyrocypris rivillii, Pyrocypris mollis, Cypridina gibbosa,* and, most remarkable, he makes the statement that *Conchoecia clausii,* a fresh-water species, gives light. If true, this is the only kind of organism living in fresh water that has been known to give out light. It seems to be an error.

*Continued from page 696, May issue.

Among others who saw the light from marine Ostracods are Claus, Chierchia, Mortensen, Hansen, Tilesius, and Döflein. The latter has made the latest and most complete study of the subject and actually described the structures of the organs through which the phenomenon is brought about. No satisfactory physiological studies have been made of the subject beyond a few rather superficial notes.

It was noted by several of the earlier observers that the light material was burned externally and, further, that it was produced in extraordinarily large quantities. Mechanical stimuli, as well as a few cases of chemical stimuli, were employed. In one case the

FIG. 1.



General view of an Ostracod crustacean. The whole group of very many sorts are remarkably alike in size and form. The integument is evaginated from the dorsal line as two lateral shells that cover the body and limbs. The black eye is seen. (After Müller.)

small animal was thrown into alcohol and the light persisted for nearly fifteen minutes. This evidently indicates that an internal light is also possible. In corrosive sublimate the creature gives one strong flash and then all is dark. Evidently the sublimate has a greater power of penetration than the alcohol. The luciferine continues to light in the water in which the animals have discharged it for a long time and with great brilliancy. When a number of the crustaceans were shaken in a vessel of sea-water one could read by the light.

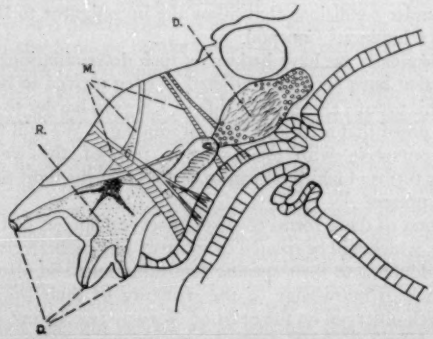
Döflein has shown much of the structure of the organ (see Fig. 2). It consists of an invaginated reservoir that opens through the upper lip of the animal through three separate ducts (*O*). Müller shows these ducts in *Pyrocypris* as seven in number, also opening through the upper lip. In Fig. 2 this reservoir is shown

by the stippled area. Its structure, or rather the structure of its walls, has not been sufficiently worked out.

At the bottom of this reservoir is a secondary invagination, the luciferine gland (*D*), in which that light-producing material is secreted. The structure and position of its constituent cells are not more than indicated, and they should be carefully studied at some future time and an attempt made to distinguish between a luciferine and a luciferase type.

The gland evidently secretes and stores up a large quantity of the material in the reservoir. This will explain the large amount that is suddenly ejected. The method of ejection is easily seen when the diagram is examined. Several bundles of muscle-

FIG. 2.




Schematic drawing of the anterior part of the head of the Ostracod *Pyrocypris*, showing the upper lip, in which are seen fine canals. *O.*, openings through which the luciferine is discharged; *D.*, light-gland; *R.*, luciferine reservoir; *M.*, muscle-fibres that compress the reservoir, and thus discharge the luciferine. (After Doflein.)

fibres (*M*) pass from the dorsal wall, of the head cavity in which the gland and reservoir lie, to its ventral wall just over the œsophagus. When these muscle-fibres contract the reservoir is put under considerable pressure and the stored secretion is forced out of the openings in the lip (*O*).

Several pigment-cells are associated with the reservoir, although they do not seem to take any part in its operation. It is possible that when the organ is active these chromatophores can be extended in such a way as to cut off any light existing inside the reservoir and prevent it from shining on the brain or other internal parts.

*Copepoda.*

The lighting of various Copepods is one of the best-known facts in our knowledge of the crustacea. The facts were reported by a number of early writers among whom are Boeck, Buckholtz, Dahl, Vanhöffen, Apstein, and Kiernik; but it was the long-continued, careful, and ingenious work of Giesbrecht at Naples that made the idea so widespread that amateur zoologists and even intelligent travellers would say "Copepods" when they saw any luminosity in the wake of a steamer at sea.

Owing to their small size and to the suddenness of the light, also to the large numbers of different kinds that are usually caught in the net at one time, it is very difficult to lay one's hands on the particular individual that has made the flash and to make it repeat the act under conditions that allow the investigator to be certain that it is a luminous Copepod.

Consequently we have had many such determinations made in the past that have been contradicted or even proved to be erroneous. This proof (a negative evidence) is even harder to establish than the proof that a form is light-producing. We will therefore content ourselves with examining a few of the well-known luminous forms in which we can be certain that the light-producing power is present.

The first of these forms consists of several species of the genus *Metridia,* which will be treated of more or less collectively because of some doubt as to their specific determinations and also because of our lack of knowledge of the structure of their organs. In 1864 Boeck observed on the coast of Norway two forms, probably *Metridia hiberinca* and *Metridia longa,* which when disturbed gave out a strong blue light. Later, Buckholtz noted a luminous Copepod which he called *Diaptomus castor,* but which was probably *Metridia longa.* They were found in Spitzbergen in large numbers in 1874. The light appeared, when the animal was disturbed, on the head and seemed to spread all over the thorax or even the posterior part of the body.

In 1875 Lilljeborg observed these creatures again in Spitzbergen in the months of December and January in the bays. His attention was called to them by the fact that the wet snow lining the shores showed numerous points of a greenish-blue light, and upon examination he found that the little waves from the bay (Mosselbay) were throwing spray and water over this snow and that the Copepods were thus deposited through its upper layers.

Of course, the snow had a temperature in the neighborhood

of the freezing-point, and the animals, being caught and held helpless, showed what the writer has often seen, a steady, somewhat weak, but long-enduring light. When free and at home in the sea they gave only a few stronger flashes when mechanically disturbed. Nearly all of the flashing forms have this same "distress reaction," and it may extend to a point where the organism is actually dead and for some time after. Its explanation probably lies in the breaking down of the vital activities by which the stored luciferine is protected from the action of the surrounding oxygen or luciferase, or both, so that the stored supply of luciferine is slowly consumed.

Vanhöffen had an opportunity to study *Metridia longa* at Karajak, in North Greenland, in February, 1893. He placed the animal in a drop of sea-water under a cover-glass and saw the lighting with a microscope. The light appeared in the posterior region of the head or on the neck (if a Copepod can be said to possess a neck). At times the light appeared to extend over the entire body. When the cover-glass was pressed with a needle the light streamed out from the body in clouds in the water. When *Metridia longa* was examined with the microscope in daylight it was seen to be colorless except for two moss-green spots on the posterior part of the head and other greenish spots on the last abdominal segment. These green spots appeared to be the light-glands. The green color appeared to be due to the color of the secreted luciferine rather than to the tissues of the gland or its surroundings.

Vanhöffen decided that the light was due to the secretion of glands, but was not certain as to whether this secretion lighted while still in the glands or only upon its discharge into the surrounding sea-water. It appeared to him that it might very well be an internal lighting, and that the streaming out of the luminous substance might be due to the pressure on the organism's body when it was squeezed between the glass slide and cover-glass and a consequent rupture of the surrounding tissues.

Knowing the uncertainty and the many contradictory reports concerning the lighting of Copepoda, Giesbrecht paid particular attention to the subject during the many years of his patient and careful labors on this group at the Naples station. As a result of these careful observations he proved that many careless or hasty reports were not founded on fact, and he definitely established

the light-producing powers of five species that are found in that region. These five species are as follows:

Family *Centropagidæ: Pleuromma abdominale, Pleuromma racilis, Leuckartia flavicornis, and Heterochæta papilligara.*

Family *Oncæidæ: Oncæa conifer.*

His method was to filter quantities of tow, that contained a medium number of Copepods alone, through a bolting cloth or other filter. As the water went through and the animals were left stranded on the filter some of them gave out sparks of light. This was best seen in the first months of the year when the filter would sparkle with numerous points of light, so bright that they could even be seen in a room in ordinary daylight. In the summer and fall, however, the light was not seen, showing that the power was developed only in the late winter and spring.

Thus we see that, as in other forms, only a few species of Copepoda can really light: four kinds out of the hundred or more that are found in the Bay of Naples that is very rich in these forms. Undoubtedly other luminous species will be discovered upon search in other waters, but to date these five and the Arctic forms, *Metridia longa* and *Metridia hiberinca,* are the only seven that can be named as having the light power. Giesbrecht was able to establish the non-luminous character of a large number of species found among twenty other genera from Naples.

Giesbrecht studied the form *Pleuromma abdominale* (Fig. 3) by isolating fresh-caught individuals on a slide in a few drops of sea-water and covering them with a cover-glass. The amount of water was such that the Copepod was not pressed upon hard enough to harm it in any way, and at the same time it was held firmly enough to keep it from changing its position easily. He found it necessary to control the conditions of light and darkness in the room because the chitenous shell was apt to reflect the daylight in such a way as to simulate a flash of autogenous light or even to mask a real display.

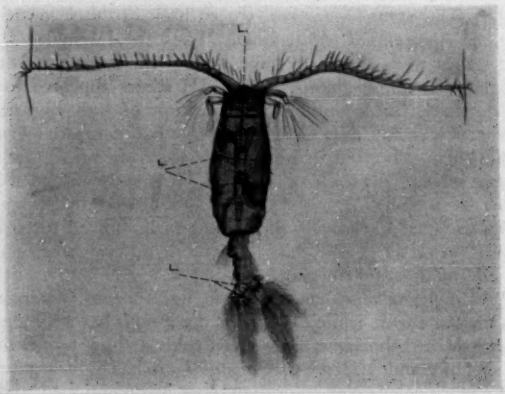
As a means of stimulation he first employed a tapping or slight pressing on the cover-glass with a needle. Then the temperature was raised and, finally, various chemical means were employed, as adding distilled water, glycerine, formol, sublimate, and several kinds of strong acids and alkalies.

Under the weaker of these stimuli he saw spots of light appear

at various points on the body, which he recognized as the points at which certain moss-green flecks appeared by ordinary daylight. Further, he recognized these spots as the seat of integumental glands, such as are common at many various points on the body of all Copepoda, excepting that they have the moss-green color only in case of their being light-organs.

When stimulated more violently the light not only appeared at these spots, but was forcibly ejected from the mouths of the glands, so hard in some cases that it lighted for some distance from the

FIG. 3.




General view of the luminous Copepod crustacean *Pleuromma abdominale*. *L.* indicates the position of some of its eighteen light-glands, which in the living animal are moss-green in color and which discharge the stored luciferine. (After Giesbrecht.)

body of the animal, as much as its own length. The light seemed green rather than blue in color.

The various light-glands were counted and located. They formed very definite organs, always appearing in the same places in different individuals of the same species (Fig. 3, *L.*). The form being studied, *Pleuromma abdominale*, has eighteen of such glands, of which only a few are shown in Fig. 3. Giesbrecht enumerated them as follows: three—one median and two lateral glands—lie close together in the forehead. Four form a pair on each anterio-lateral corner of the second thoracic segment. Four

more appear as a pair on each posterio-lateral end of the anal segment, a pair is found on each side of the distal part of the furca, and a single organ is placed just above the pigmented organ. Two more appear on the under side of the head near the organ of the mandibles.

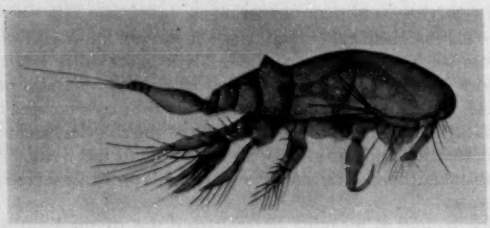
These glands were fairly large, pear-shaped, and lay close against the shell. Unfortunately they were not studied in sections as to their cellular structure and nerve and blood supply. The number and arrangement of the light organs were exactly alike in both sexes. In all of the luminous forms the light-organs went back into the earlier stages, as is common in crustaceans and insects. The organs were best traced back in the several larval stages of *Pleuromma abdominale*. Thus the IV and V Copepodid-stages were shown to have exactly the same number and arrangement of light-glands. The I–III stages appeared to have very much the same number and position of light-organs, but Giesbrecht was not quite satisfied that he had correctly seen and counted them. He felt that all glands were not present in these younger stages. In the first week in January he found a large number of Nanplins stages that seemed to belong to *Pleuromma abdominale* or *Pleuromma gracile*, and each showed three light-organs: one on the forehead, as in the adult, and two small ones on each side of this median gland.

*Pleuromma gracile* has seventeen light-organs, arranged in much the same way, while *Leuckartia flavicornis* has only ten. All of them showed the same moss-green color and are evidently the same sort of gland. *Heterochæta papilligera* has light-organs that are of a much paler green color than those just mentioned, and also the glands seem to be almost entirely emptied when the animal is first caught and picked out for study under the microscope. Therefore, it was not possible for Giesbrecht to count the glands or study their operation. This species seemed to have more than eighteen, however. They appeared to be arranged in pairs and groups that either possessed a common duct or had their single ducts very closely placed together. Some of the glands were located as follows: two pairs in the head, with ducts opening laterally; three glands on each side in the anal segment; one in the furca; three in each basal joint of each antenna; two in the distal part of each maxilla; two or three in the third joint of the second, third, and fourth swimming foot, besides a number of others in different parts of the body.

*Oncæa conifer* (Fig. 4), a form belonging to an entirely different family, showed a quite different appearance and arrangement of the light-glands. They were more irregular and larger, with shorter ducts in the head, while those in the abdomen possessed longer ducts and were still larger. The size varied with the condition of fulness or of exhaustion of the secretion. Also the light material (luciferine), which seemed to consist of large droplets of a greenish oil in the above forms (Centropagidæ), was here of a granular nature, as seen *in situ* in the living animal. Furthermore, the light which was decidedly greenish in the former described animals, was of decided blue in this case.

Only the secretion of the body glands lighted in *Oncæa*. Those on the limbs did not. Nor were the light-glands segregated into

FIG. 4.



Lateral view of the luminous Copepod, *Oncæa conifer*. (After Giesbrecht.)

groups, but were scattered all over the surface of the body, especially the back. They were much more numerous than in any of the other forms, although they were not counted as exactly as could be wished. At least thirty were present on the head alone, and the total number must have been more than seventy in all. More were present in the larger female than in the male.

We still lack any idea of the cellular structure of these glands. Giesbrecht considered them to be physiological modifications of the integumentary glands that are numerous in the Copepods, and is probably quite right in this idea. It would probably not be difficult to see them in total specimens that had been fixed in any picric-acid fixing fluid and stained in bulk in carmine or picric-hæmatoxylin. Nor would it be difficult to cut sections, in the writer's opinion, and to see their structure with iron hæmatoxylin or any

other of our best stains. This would be one more of the many interesting pieces of work to be done to enlarge our knowledge of the luminous animals.

Giesbrecht found that it was quite easy to place these five sorts of Copepods upon a bit of dry filter-paper and to dry them out in a current of air in a window without the loss of the light secretion. He kept them dried in this way, and days or months afterwards was able to moisten them and see the light reappear. He could also keep them, dead, for some time, in glycerine and then, by placing them in sea-water, again get the light. The secretion consisted, as above stated, of greenish-yellow droplets or of granules, all of which appeared homogeneous. They were not any form of living protoplasm, but a lifeless material of specific chemical composition which retained its power to light after the death of the tissues, and especially after being kept in a dry state.

Giesbrecht made many experiments by treating the secretion with common chemicals. But, since he did not know of Dubois's experiments and discovery of the catalytic agent called luciferase, his work in this line has not sufficient value to form a part of this treatise. He did note the fact that each of the green-colored light-glands lay in the neighborhood of some of the colorless and undifferentiated integument glands, and it seems to the writer highly probable that those same integumental glands probably secreted the luciferase.

The biological meaning or ecological use of the light to the Copepods was well stated by Giesbrecht. He noted that it cannot be a sex lure through the eye, because, while some of the seven luminous species have very small eyes, the majority have no eye at all. It is probably used as a sacrifice lure. The animal, when disturbed or attacked, shoots the light-cloud out and then swims away, leaving the fast-disappearing light material to claim the attention of its enemy while it escapes itself. It can hardly be a warning signal, as all of the copepods are readily eaten by certain other animals.

One group of broad, flat Copepods, the family Corycædiæ, are noticeable for the magnificent color that is found on parts of or on all of their bodies. The best-known member of this group is the species *Sapphirina ovatolanceolata*, a pelagic species that is common in the waters of the Bay of Naples. The color of this and the allied forms is due to diffraction phenomena caused by the

structure of the integument. As they move, the reflected light appears in all the colors of the spectrum, and one sees them sparkle with everchanging hues of green, gold, blue, violet, orange, etc. Several writers have mistaken these brilliant colors for autogenous light, and some serious descriptions have been written of this phenomenon in that error. Such a mistake is easily made, as can be seen from the following: Some graduate students of Princeton University took another species of this group in the tow at Montego Bay, on the Island of Jamaica. While going over this tow at night by weak lamplight to pick out all luminous forms for the writer, they took this animal for a lighting form, because, at intervals, it gave out a bright orange to ruby-red light from its posterior end. Upon examining it carefully in Princeton during the following winter, after it was preserved in formol and alcohol, it was found that the " light " was still present. In this organism the diffractive structure was present only in two of the large, flat appendages of the tail, and as the creature swam and turned, they shone by the reflected light, whenever the angle was right between the lamp, the object, and the observer's eye. Under the microscope they could be turned in a glass tube so as to show the most beautiful and brightest colors. We have in these organisms some of the most deceptive resemblances of a real autogenous light production.

*Schizopoda.*

The Schizopoda form a group of the higher crustacea, being one of the suborders that compose the lower half (in morphological value, but not in numbers) of the order Podophthalmata, of which the familiar sub-order of Decapoda form the higher part. There are two families of the Schizopoda, the *Mysidæ*, which have no luminous members, and the *Euphausidæ*, many of whose members are light-producing. It is with these that we will deal in the following pages.

There are many species of these medium-sized, shrimp-like animals, and they are found in all seas, mostly leading a pelagic life, some few on the surface, many more in depths of from 25 to 1000 metres. They are commonest near the bottom and in intermediate depths of about 300 metres.

One of the earliest observations made on these animals was that most of the forms were provided with a number (ten) of

round, pigmented, eye-like organs placed on the first four abdominal segments between the bases of the swimming legs, as well as on the underside of the thorax and on the eye-stalk. From their rounded shape and the presence of a lens, an iris-like opening, and many other features, these organs were taken to be simple eyes, like the ocelli of insects, and they were called the "accessory eyes" by many naturalists, including such specialists in the crustacea tribe as Claus, and others as well known. It was the practical experience in the field obtained during the *Challenger* Expedition that led Sir John Murray and G. O. Sars to learn that these were not organs to receive light (an eye), but that they were organs to produce and discharge light—real light-organs. Patten erroneously clung to the idea that these were real eyes as late as 1886.

Since that time papers have been written on the structure and physiology of these organs by Vallentin and Cunningham (*Nyctiphanes norvegica*), Chun (several genera), Giesbrecht (several forms), Hansen (several genera), Illig (*Gnathophausia*), Trojan (*Nyctiphanes conchii*), and others.

Taking advantage of these several careful investigations, the writer will attempt to generalize and describe the general principles on which these organs are constructed, with some reference to their origin and development and their use in the several forms.

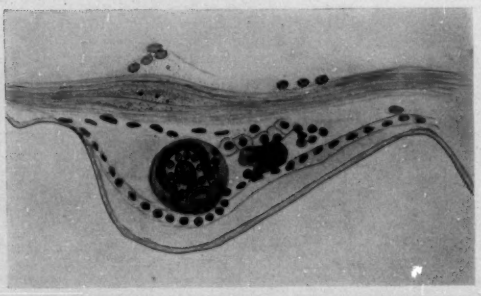
In the majority of the luminous forms the organs are ten in number and are distributed as follows: Two are found, one each on the outer portion of the eye-ball or eye-stalk. The outer surface of this organ is flush with the general surface of the eye. Four occur as two pairs placed on the lower outer edge of the thorax—one pair near the origin of the second thoracic feet, and the second pair near the origin of the seventh pair of thoracic feet. These round structures protrude for more than half their diameter from the general surface of the body. The remaining four photospheres, as these organs are called, are placed on the median ventral surfaces of the first four abdominal segments, between the bases of the swimming legs. Each of these latter organs is placed directly under and partly imbedded in the substance of the nerve-ganglion belonging to the segment on which it lies. Fig. 5 shows this condition.

This arrangement holds for the large majority of luminous *Euphausidæ*, and we do not find any form that possesses more

than the ten organs noted above. On the other hand, there are many that show a smaller number, running down to only three in the genus *Stylochiron*. In cases where the organs are less than ten in number the first organ that is missed appears to be the posterior abdominal organ. When several abdominal organs are absent in any form, then the first or most anterior pair of thoracic organs also are not developed. The eye-organ appears to be absent only in extreme cases, as in some species of *Stylochiron*. Fig. 6 shows the lights as they appear in *Nyctiphanes norvegica* during their living activity.

In the structure of the organs we find two types in nearly

FIG. 5.



Lateral view of an abdominal light-organ or photosphere of *Nematoscelis mantis* to show its relation to the nerve ganglion. (After Chun.)

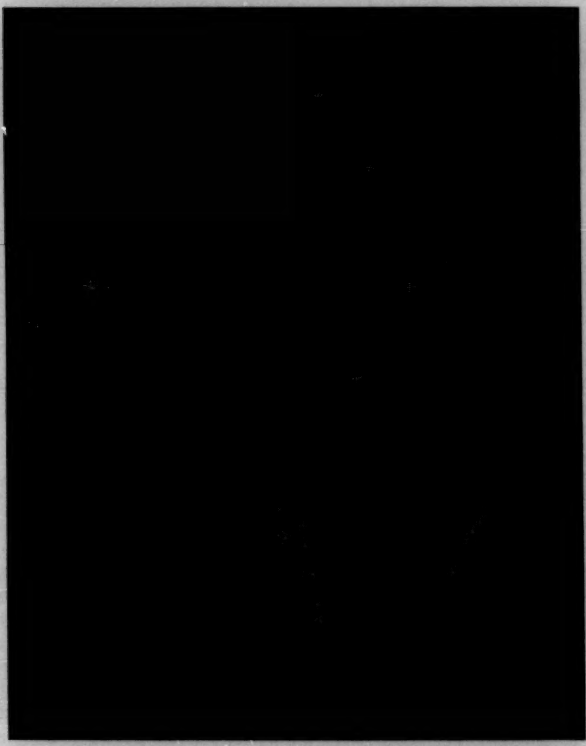
every species. First, and for certain reasons the most primitive, is the type of organ found on the eye-stalk. Secondly, we find, as a more specialized type, all the other organs, which are practically the same in size and structure in any given species. These thoracic and abdominal organs are more highly differentiated than the eye-stalk organs.

Fig. 7 and Fig. 8, A and B, show one of these eye-stalk light organs from *Nematoscelis rostrata* and two stages of the same organ from *Stylochiron mastigophorum*. We will consider the various layers and structures from the proximal, rounded end of the organ outward.

The first region that is noticeable, especially in life, is a thin

layer of pigment, of a color that is usually Cinnibar red in these species from deeper water, but that is red-brown or even black in

FIG. 6.

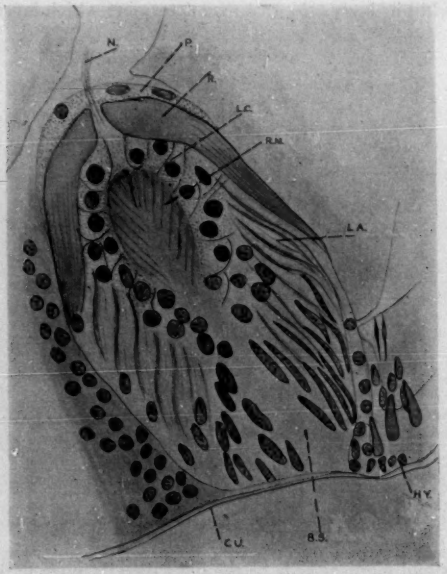


Drawing of *Nyctiphanes norvegica*, swimming about some gulf weed that has drifted in by a stone pier. (Drawn by Bruce Horsfal after descriptions by the writer.)

some of the species living inshore or in shallower waters. This layer is composed of flat polyhedral cells (*P.*) and extends distally

about half the length of the organ, or as far as the real reflector extends. It appears to be a mesodermal structure, and its cells and nuclei can be seen to form a transition at the edges into the mesodermal connective tissue of the stalk. The pigment is very delicate in most of the forms and is seldom preserved in the usual fixa-

FIG. 7.



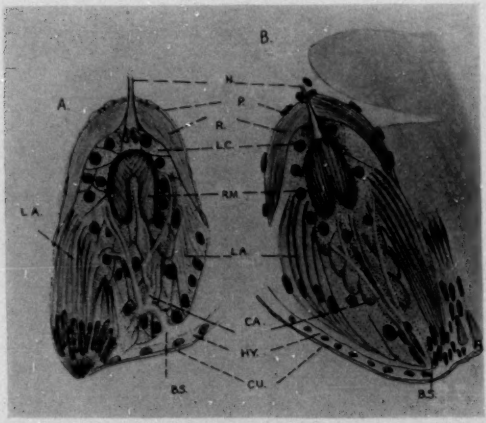

Drawing of a section through the longitudinal axis of the eye-stalk light-organ of *Nematoscelis rostrata*. *N.*, nerve; *P.*, pigment; *R.*, reflector; *L.C.*, light-cells; *R.M.*, rod mass; *La.*, lamellæ; *Ca.*, capillaries; *Hy.*, hypodermis; *Cu.*, cuticle; *B.S.*, blood-sinus. (After Chun.)

tives. The form of the cell-bodies remains, clearly seen, however, and can be distinguished clearly in Flemming and other good preservations.

Directly distad of the pigment layer comes the reflector (*R.*), which also appears to be mesodermal in origin and forms a thick refractive layer enveloping the posterior half of the organ. It

forms a deep, narrow cup or a somewhat wider, shallower one, according to the species, or to whether it is an older or younger specimen. Its tissues are for the most part composed of waved strands or plates of some dense, deep-staining substance that is not guanin, and it loses most, but not all, of its reflective power when treated with the usual reagents and mounted in balsam. Its distal edge is thinned down to a sharp rim, and no nuclei are to be found in its body. Nor can we determine which layer of cells,

FIG. 8, A AND B.




A younger (A) and an older (B) eye-stalk light-organ of *Stylochiron mastigophera*. Lettering same as in Fig. 7. (After Chun.)

the proximal pigment-cells or the next distal (inner with respect to the organ) layer of cells, is responsible for its origin and maintenance.

The next distal or inner layer of cells are thick, heavy gland-cells with strong, working nuclei. Their cytoplasm is filled with a granular material, and they are without doubt the specific cells of the organ, the luciferine-secreting cells or light-cells (*L.C.*). They form a single layer in nearly all cases, although sometimes they may lie obliquely over one another so as to form two layers

in places. As an evidence of their function and importance they are supplied by nerve-fibres and with a large, well-distributed blood supply. The large single nerve (*N.*) approaches them from the proximal end of the organ, where it penetrates both pigment layer and reflector and its branches spread and divide, to be lost among the individual cells. The blood supply, on the other hand, approaches from the opposite or distal pole of the organ as a large vessel that divides and spreads radially, to also end as fine branches that pass as a plexus of capillaries among the light-cells (*Ca.*). The return of this blood is probably in the same direction through another vessel into the large distal sinus that will be described below.

The inner surface of the cup-shaped layer of light-cells is in contact with the outside of another cup-shaped structure, the rod-mass (R. M.), which here seems to be a distal outgrowth of the main body of light-cells. The rods that compose this body are mostly directed in a parallel direction, distally, and they present an optical appearance that leads one to suppose them to be organs of refraction. In some of the organs of this type, especially the organs of larval stages, they appear to extend to the distal surface of the photosphere, and to the writer they seem to be a modified chitenous secretion of the light-cells. They thus stand, as one factor, in the evidence that these light-cells were invaginated from the hypodermis and that they thus have, in common with most other light-cells, an ectodermal origin.

There are still several puzzles to solve as to their use in the organ. The distal cells of the light-organ pass over their edge and appear to fill the hollow of their cup-shaped body.

We now have to deal with the most peculiar structures in connection with the organ, the lamellæ (*La.*), as they have most often been called. These are a series of strong strands or plates that form a circular collar extending from the external chitin of the eye-stalk down to the distal edge of the cup-shaped reflector. In fact, in many, or even in most, forms they appear to be a part of the reflector. Trojan has called the structure the "external reflector," but the writer cannot agree with this. While they are also dense and refractive, they still show differences of appearance and of staining power, and in one point at least we can be clear: they are of direct epidermal origin. There is a clear and direct transition of the general outer hypodermis of this part of the eye-

stalk into these cells in the eye-stalk organs, and they are also continued into the hypodermal cornea that covers the outer face of the organ. Fig. 8A, shows this with especial clearness. Their nuclei are very large, somewhat elongate to fit the spaces between the lamellar rods, and form a direct row continuous with the nuclei of the hypodermal cells.

A blood-sinus (*B. S.*) of some extent lies between the outer surface of the light-cells and the external cornea in *Nematocelis* but is poorly developed in *Stylochiron*. The latter is, therefore, the more primitive in structure of the two forms, and also the most primitive of any of this class of light-organs that we know. We can but speculate as to the first origin of this type of organ. An invagination to form the light-cells, the formation of the

FIG. 9.

Lateral view of *Nyctiphanes norvegica*. The positions of the light-organs are indicated by black dots. Three of them, one eye-stalk organ and two thoracic organs, being on the other side, are not represented. (After Watasi.)

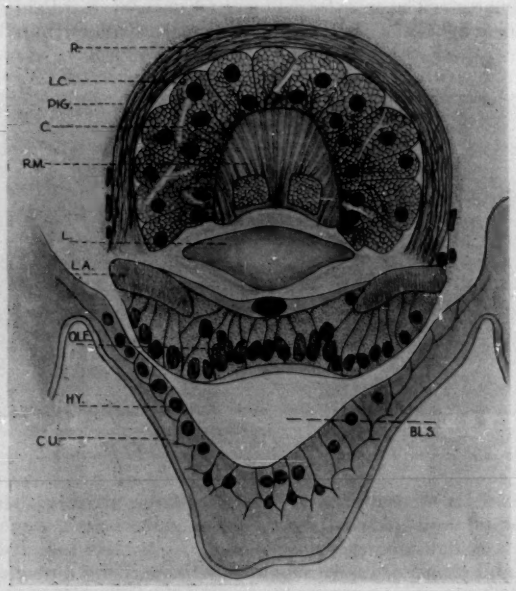
external cornea by the closing of the opening and the lengthening of the peripheral hypodermal cells some distance from the original point of invagination to form the lamellæ, is the most probable course of events in this process.

Let us now turn to the other type of photospherium as seen on the thorax and abdomen of these animals. We evidently see here an organ that is built upon the same ground plan, but which has had other accessory structures added to it and has had some of the original structures changed to meet the new conditions. Fig. 9 shows a lateral view of *Nyctiphanes norvegica*, with the organs shown as black dots.

The abdominal light-organ of *Nyctiphanes norvegica* has been studied by many and is probably one of the most highly developed and characteristic photospheria in the group. The corresponding organ of *Nematocelis mantis* will serve to show a photospherium of the simpler structure in this type. Fig. 10 represents a section of the light-organs of *Nyctiphanes norvegica*,

and Fig. 11, A and B, shows sections of the abdominal light-organs of *Euphausia gracilis* (A) and *Nematocelis mantis* (B). In general it can be remarked that these organs have not only become more differentiated, but that the whole structure has assumed a more compact and rounded shape and has grown to be partly

FIG. 10.




Section of a photospherium of *Nyctiphanes norvegica*. *Pig.*, pigment-layer; *R.*, reflector *L.C.*, light-cells; *C.*, capillary; *L.*, lens; *La.*, lamellæ; *O.le.*, outer lens; *R.M.*, rod mass; *Hy.*, hypodermis; *Bl. S.*, blood-sinus; *Cu.*, cuticle. (Drawn by E. Grace White from a preparation.)

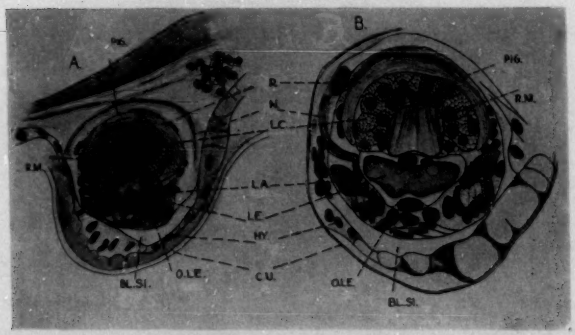
freed from the surrounding tissues, partly because of large intervening blood-sinuses and partly because of more sudden transitions between the tissues of the organ and the general body tissues.

Beginning with the proximal part, we find the same layer of pigment (*Pig.*) lying on the outside of the cup-shaped reflector

(*R.*). There is practically no difference between their structures as seen here and as seen in the eye-stalk organ, except that the "cup" is usually wider and shallower in the second type of organ now under consideration. Nuclei are present in the pigment-layer, which here is composed of two or three layers of flat cells with large, flat nuclei. No nuclei can be seen in the body of the reflector, and it is still a question if this structure is formed by the pigment-cell layer or by the inner (distal) layer of light-cells.

These light-cells (*L. C.*) present no real difference from those

FIG. 11.




Sections of the abdominal light-organs of *Euphausia gracilis* (A) and *Nematocelis mantis* (B). *Pig.*, pigment-layer; *R.*, reflector; *R.M.*, rod mass; *N.*, nerve; *l.c.*, light-cells; *La.*, lamellæ; *le.*, lens; *o.le.*, outer lens; *bl. si.*, blood-sinus; *Hy.*, hypodermis; *cu.*, cuticle. (After Chun.)

described for eye-stalk organ. The same large, active, glandular bodies and semi-epithelial arrangements of the units are shown, as well as the same character of nuclei. We see, too, a well-developed plexus of capillaries running between and through the cells. The layer is supplied with nerve-endings from fibre-trunks that approach it, not from the extreme proximal pole of the organ, breaking through pigment and reflector, but by several smaller trunks that reach over the edge of the reflector cup to enter and branch out in the light-cell layer (*N.*).

The fibrillar mass or rod mass (*R. M.*) is also present and well developed. The rodlets that compose it show several minor differences in the various species. Thus in *Nyctiphanes* it shows several

combinations of directions of the rods, while in *Nematocelis* it is made up of rods all lying parallel to one another in a proximo-distal direction. In *Stylochiron* the rodlets are arranged radially to form a perfect sphere.

The first new structure to be observed is a very perfect chitenous lens (*Le.*) placed on the distal opening of the light-cell cup and against the fibrillar mass. In form this lens varies from round, as in *Euphausia gracilis*, through various lenticular shapes to irregularly flat, as in *Euphausia pellucida*. The inclination is, however, in most cases, toward a real lens-shape that will focus the light at short distance from the animal's body.

This lens has been mentioned as chitenous. Its composition has never been adequately worked out. It shows a color and staining reactions that seem to warrant one in calling it chiten. It also shows zones of fixation that make it appear that the body is of a soft or even semi-fluid condition in life. In most of the forms of Euphausidæ the cells that form the lens are easily discerned in sections as a layer of large, flattened cells with correspondingly large and flattened nuclei. In *Nyctiphanes norvegica* this layer is very hard to see and appears to have lost its cellular nature. The origin of this lens and the morphological meaning of its controlling cell-layer are very puzzling. Practically no trace of it occurs in the eye-stalk organs unless certain cells of the light-cell mass lying outside of the reflector cup and against the lamellar ring are the analgen of this structure. Or, again, we would seem to be obliged to consider the lens as the result of a secondary invagination from the outer surface, with the cells of this infolding layer secreting the chitenous material from their distal surfaces. It appears certain that the presence of this lens divided the mass of light-cells into the proximal cup of real light-producing cells and a distal mass whose staining reactions and cytoplasmic structure show a differentiation that indicate their non-participation in the light processes.

Trojan considers these cells just outside the lens to be an external layer of light-cells in *Nyctiphanes conchii*. His figure certainly shows very little difference between them and the real light-cells. In other forms, however, especially in *Nyctiphanes norvegica*, real differences appear, and one cannot but come to the conclusion in this latter case that these outer cells have become differentiated into a secondary lens or outer lens (*O. Le.*).

In *Nyctiphanes norvegica* these cells have become arranged in a well-defined circular layer of definite thickness. At the outer edge this layer has been cut away to insert the ring of lamellar tissue (*La.*), which is still quite distinct from the reflector against which it lies. The position of this lamellar layer is very suggestive of a possible new function. Trojan and others have called it the outer reflector in the simpler organs. In its position and the direction of its lamellæ or rods in *Nyctiphanes norvegica* it strongly suggests a muscular focussing arrangement. This view can be easily proved or disproved by the proper staining and other tests to determine if the lamellæ are muscle fibrilis or not.

Outside of the secondary lens and between it and the hypodermis of the cornea comes a large blood-sinus (*Bl. S.*). The connections of this sinus and those of the strong capillaries that enter the light-cell layer have not been traced. This blood seems to be the only layer between the light-cells and the exterior that is not specialized for the transmission of light by being made transparent.

The cornea is merely a somewhat thickened portion of the hypodermis with its cuticle. It has been rendered transparent for the passage of the light. The uses of this light are somewhat obscure. But few real observations have been made, and some interesting speculations. Dr. William H. Dall, of the National Museum, has observed some Euphasid, probably *Nyctiphanes*, coming in vast swarms to the surface at night in the waters of Puget Sound in April, probably for purposes of breeding. They were lighting continuously and made a considerable luminosity in the water. Here it seems that they used their light in numerous flashes as a mating signal.

The writer has seen them swarming at the surface in much the same way, on the surface and on the shores of Passamaquoddy Bay, in Maine, in latter July and August. This species was *Nyctiphanes norvegica*, and the animals were giving out flashes that were nearly as bright as a fire-fly. Fig. 6 was drawn from descriptions of this scene. The nerves supplying the organs were evidently used to cause and control these flashes. Miss Mildred Prince has also told the writer how these fall swarms of the same animals were thrown ashore in windrows on the beaches of Campobello Island, in the same region. These masses of animals were glowing continuously, when disturbed, with a weaker light than that shown by the flashes. This abnormal lighting or

"death-glow" is characteristic of many creatures and shows a weakness or disorganization of the nervous powers.

Chun discusses the light process and shows that it might be possible that the animal uses it to see its prey or other objects, since with the abdomen flexed all of the lights would converge on the region directly in front of the creature. He also calls attention to the fact that some of the photospheria, especially the abdominal organs, are capable of being moved in an anterio-posterior direction through a considerable arc by their possessor.

The animal is not always easy to stimulate into the lighting condition. Sometimes a mere jar of the vessel of water in which they are will bring about a display. Usually, too, they light when removed from the water with the hand. At other times, however, one can jar or annoy them for a considerable time without seeing the light. When crushed or severely injured the steady "death-glow" sets in. This can also be brought about by more minute injuries to the nerve-ganglia with a needle.

We must now examine one of the lower forms of Schizopoda, *Gnathophausia calcarata*, captured by the German deep-sea expedition in 1898, at a depth of 1326 metres. This form gave off a greenish light from about the mouth region. Illig observed that, when it was thrown into a picric-acid fixative, the luminous secretion was fixed in whitish strings by the preservative action of the fluid.

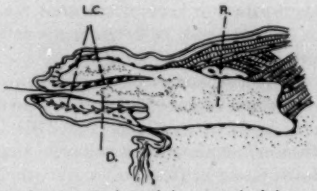
He detected the exact point from which the secretion came, and found it to be a papilla situated on the base of the exognath of the second pair of maxillæ, one on each of the pair of limbs. He cut longitudinal sections of this part and pictures the gland as seen under the microscope. Fig. 12 is copied from this drawing of Illig's.

The section shows an invagination into the body of the papillæ, passing through the length of the papillæ as a duct (*D.*) and expanding in the larger basal portion into a large, glandular reservoir (*R.*). The walls of the duct are of the same type as the external integument, a substantial hypodermis bearing a somewhat thinner cuticle. At the opening of the reservoir into the duct the cuticle is folded back, forming a peculiar, valve-like arrangement, the use of which is hard to determine. It is possibly of use in retaining the luminous fluid until the time of discharge.

The reservoir is large and of sac-like shape. A clotted sub-

stance, resembling a blood-clot in Illig's figure, occupies the interior. The wall is made of a thin layer of flat cells with flattened nuclei, the whole somewhat resembling the intima of a blood-vessel. The glands that secrete the luciferine (*L. c.*) lie in the walls of the papilla through which the light substance is ejected. But they do not open into the duct, but into a crevice in this wall that passes backward and discharges into the reservoir behind the valve-like edge of the opening from reservoir into duct. Illig has not described these glands carefully. His figure leaves one in doubt as to whether they are unicellular glands, which are almost unknown in crustaceans, or whether they are bunches of gland-cells arranged in the form of the usual integumentary

FIG. 12.




Section of the light-organ found on the base of the exognath of the second pair of maxillæ of *Gnathophausia calcarata*. *l. c.*, light-cells; *r.*, reservoir; *d.*, duct. (After Illig.)

glands of these forms. The latter seems the more natural, and further work will probably demonstrate that it is the case.

### *Higher Decapod Forms.*

The middle depth of the ocean, from 600 metres to 2000 metres in depth and over, are the home of a large number of small- to medium-sized decapod crustaceans, called prawns in general and living a free swimming life near the bottom or suspended at these depths over much deeper bodies of water. In color they are either transparent or of a bright red, in part or in whole, while a few of them show bright-blue markings on parts of their bodies.

Many of these prawns are capable of producing light, and here we find, as in the Schizopoda, two types or perhaps three. One type with an external combustion, one with an internal combus-

tion, and a possible third in which the light-producing is a combination of these two forms.

The first group of prawns consists of several known species, and in all probability a number of species yet to be determined, that, when disturbed in the water in which they live, throw out a stream of luminous substance from two points at the bases of the second pair of antennæ, as it has been described by several naturalists. Alcock mentions two such prawns, *Heterocarpus alphonsi* and *Aristeus coruscans*, both of which poured out copious clouds of a "ghostly blue light of sufficient intensity to illuminate a bucket of sea-water so that its contents were visible in the clearest detail." Alcock thought that the light came from the orifices of the nephridia or "green glands." Recently, through the kindness of Dr. H. F. Moore and Mr. W. W. Welch, of the United States Fish Commission, the writer has been given the privilege of examining some as yet unnamed species of prawns, much resembling those described by Alcock, that were taken from the waters of our eastern coast in depths of from 300 to 1000 metres. These creatures were placed in large glass jars of sea-water when brought on the vessel "*Grampus*" at night, and when disturbed they gave out the same clouds of bluish light. As in the case mentioned by Alcock, these two streams of luminous material were copious and appeared to come from the "under side of the head." Fig. 13 shows them as they appeared under these conditions.

The writer has dissected and sectioned these prawns and come to the following conclusion: The luciferine is secreted by a large number of glands of the common integumental type found in crustaceans. These glands pour out the secretion from hundreds of tiny, hair-like ducts opening on the under side of the head from around the mouth and from the inner sides of the bases of the limbs on the anterior part of the thorax. This very small amount of secretion is then mixed with the strong stream of water, augmented for the occasion, that comes from the respiratory chamber and is thus carried out in the copious clouds of light that have been described. Fig. 13 shows some of these prawns as they appear when the light is emitted. Mr. W. W. Welsh told the writer how the discharge sometimes came forth as two rings like the rings blown by a man smoking. These rings moved through the water with their vortex-momentum and ended by sticking

against the sides of the glass vessel, still ring-like, where they remained luminous for some time.

The glands (Fig. 14) consist of from three to five or seven cells (in section) placed closely together around a very small lumen that empties out through a fine, hair-like duct. This duct joins the others that come from the neighboring glands of the group and runs parallel with them, forming all together a large body of separate canals, so fine that their exact structure has not been made out. They all open separately through fine canals in the chiten of the shell.

FIG. 13.

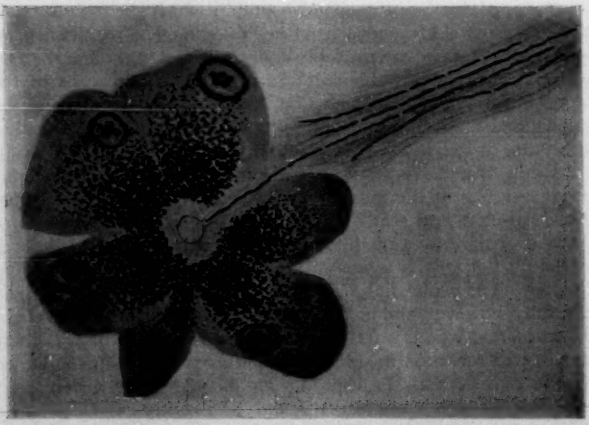
Representation of the two prawns (like *Heterocarpus* or *Aristeus*) as they appear when lighting in the sea. (Original drawing by E. Grace White, after descriptions by Alcock and W. W. Welsh.)

The gland-cells appear to be of several different types on account of their size and the character of the contents of their cytoplasm. Each cell has a large proximal surface, forming a portion of the outer surface of the spherical gland, while its exceedingly small distal surface forms a part of the tiny lumen and fundus of the gland. The nucleus is somewhat proximal and the cytoplasm is divided into one or more zones, according to the type of the gland and the state of its activity.

First we find what the writer considers to be a young gland, either in actual age or in its cycle of secretory activity. The cytoplasm is homogeneous in color and texture, except for a striated appearance that reminds one of the muscle or of some electric tissues. This gland is very small and apparently is not secreting; it stains dark red in a Delafield-eosin preparation.

A second type is possibly the luciferine gland. It is much larger than the young gland, and its cytoplasm is composed of a

FIG. 14.



Drawing of a light-gland of a deep-sea prawn (species undetermined). Shows six cells around the lumen, dark granular secretion in cells, and the duct of this gland passing out to join a group of ducts from other neighboring glands. Ducts are only visible when the secretion is in them and is stained. (Original drawing.)

pink proximal portion and a distal portion filled with fine, deep-staining granules. Fig. 14 shows this particular kind. The extreme distal portion of the cell is more or less free of the granules and is modified by the presence of fine channels opening into the lumen, which is very small. The granules pass from the secreting zone through these canals into the lumen and thus out of the gland through the long, fine ducts. These ducts are so fine that but one granule at a time can pass into the lumen. They are only visible when occupied by a row of the granules and when the granules

are properly stained. The bundle of ducts separates considerably upon approaching the surface from which they discharge. Each separate duct passes between the hypodermal cells and opens to the exterior through a small canal through the chitenous cuticle.

Others of the glands are large, and the cytoplasm of the cells is somewhat granular but almost colorless with this stain (Delafield's hæmatoxylin and eosin). It is probable that such a gland is in some stage of secretion in which the staining power is temporarily lost. The exact relationship is not clear. The cells stain a very light pink.

A fourth kind of this gland is one in which the cytoplasm of the cells is of a homogeneous, clear-blue material that resembles mucus. Such cases are probably a mucus-gland, although the fact was not positively established. In some cases both cells of the blue (mucus) and light pink kinds were present in one and the same gland. This did not seem to indicate a transition, but rather a mixture of two kinds of cells in one gland.

While the above structures are in all probability the light-producing organs, the possibility yet remains that the nephridial glands are the real seat of the luciferase production. The production of light by a modified portion of a renal gland is known in the fly *Bolitophila luminosa*, as will be shown in a succeeding chapter. The nephridial gland of this shrimp has been examined carefully, however, and no specialization of its epithelium has been observed that would warrant such a supposition. Nor was there any clotted secretion in its lumen such as is visible in the lumen of the characteristic light-producing glands. The writer feels confident that the integumental glands as roughly described above will prove to be the seat of light production, and that the squirting action observed in the living organism will be found to be due to the action of the respiratory stream in carrying the luciferine out into the regions in front of the creature's head.

The next forms to be studied are the decapod forms as exemplified by the genus *Sergestes*. In general appearance and in habit as well as in size the species of this kind closely resemble the above forms. Dr. Stanley Kemp has worked up the forms belonging to the Natantia and finds that we know of six species that bear light-organs of the internal type, as follows:

*Penæidea: Sergestes challengerii and Sergestes gloriosus.*

*Caridea: Acanthephyra pellucida, Acanthephyra debilis, Hoplophorus grimaldi, and Hoplophorus sp. juv.*

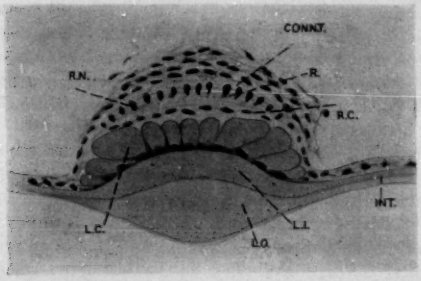
and that, further, it is probable that two other species belonging to the Penæidea, *Gennades* and *Amalopenæus*, also possess light-organs of the same general type. All these animals are very rare and are only occasionally captured by more or less expensive expeditions, and investigators should take the trouble, when so fortunate as to be on an expedition and see them caught, to observe their light powers at once in a dark room and to preserve some of them for histologic investigation in the laboratory.

*Sergestes challengerii* shows a great many—as many as one hundred and fifty—photophores on the surface of its body. The smaller and younger specimens show a lesser number, showing that the number increases with growth until maturity. These organs are distributed, according to Kemp, somewhat as follows: "They occur on the lower sides, on the oral appendages, on the thoracic and abdominal sterna, on the ventral surface of the outer uropods, and on many of the leg-joints. All are so situated that the light which they produce is thrown directly or obliquely downward." Some organs have been described on the lateral face of the carapace. These are not on its outer surface, but are placed on its inner surface when it is infolded, to shine downward and illuminate the gill-chamber from above. They are small and the lens varies from 0.06 mm. to 0.14 mm. in diameter. They are all practically the same in their structure, which, however, differs greatly from that of the photophores (photospheridia) of the Euphausidæ.

Figs. 15 and 16 show representations of two of these organs, Fig. 15 being a drawing of one from the penultimate joint of the second maxillipede and Fig. 16 a drawing of one of those found on the outer wall of the gill-chamber. The outer structure is a very perfect cuticular lens (*L. O.* and *L. I.*), being a thickening of the chitenous cuticle of the body. This lens is bi-convex and is composed of two layers that stain somewhat differently and represent the layers shown by other parts of the body cuticle. This modified cuticle is made very transparent, as would be expected, and it will be interesting to ascertain its index of refraction in the living of fresh state and to compute its focus as used by the animal. The chief portion of this lens-thickening is formed by the

outer layer (*L. O.*), which is bi-convex. We should also learn how this region is carried through the process of ecdysis.

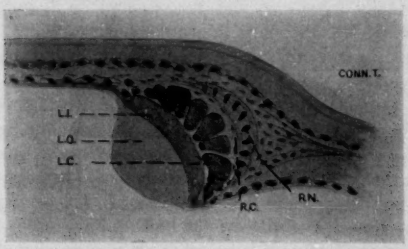
FIG. 15.




One of the larger light-organs of *Sergestes challengerii* in median vertical section. *l.o.*, outer part of lens; *l.i.*, inner layer of lens; *l.c.*, light-cells with distal nuclei; *r.c.*, reflector-cells; *r.*, reflector; *r.n.*, nuclei in reflector; *conn. t.*, connective tissue at back of organ. (After Kemp.)

The layer immediately below or proximal to the lens is obviously a modified portion of the hypodermis (*L. C.*). The cells have become very much larger, particularly their proximal

FIG. 16.




Another light-organ from *Sergestes challengerii*, found inside the gill-chamber on the integument. Lettering same as in Fig. 15. (After Kemp.)

parts, and the cytoplasm has assumed a strongly refractive, hyaline appearance that does not give any clue to their use. In properly preserved specimens as well as in fresh specimens these cells

contain a deep, transparent, blue pigment which is the cause of the blue color of the photophores in the living or freshly-dead animal. This further complicates the question. These cells are the only ones in the structure that appear to have glandular cytoplasmic bodies capable of secreting luciferine. And yet the presence of the blue pigment would indicate that they were accessory structures rather than the specific cells of the organ. And Kemp has called attention to the fact that this layer of cells also forms a lens-shaped mass which might indicate a refractive function. This idea does not appeal very strongly to the writer, who is inclined to believe that they are the light-producing cells which also serve to tinge the light with the blue color. The fact that they are apparently the only ectodermal cells in the organ also lends strength to this view.

Their nuclei occupy a very remarkable position, being situated in the extreme distal tip of each cell. Kemp describes, although he does not figure, chromosomes in these bodies. We must also consider that these cells are the only ones in direct contact with the lens, and that, therefore, they must be the cells that secrete this lens. They are, apparently, cells with at least three and possibly four functions to perform.

Just under these light cells appears a thin and unimportant appearing layer of flat, very thin cells that serve to separate the light-cells from the reflector. These flat, thin nuclei appear in the section as lines. It is not possible to assign any function to this layer until further material has been secured and more complete studies made. They will be called temporarily the reflector cells (*R. C.*).

Proximad to the flat cells appear a thick, dish-shaped layer which has been called by Hansen the reflector (*R.*). Kemp agrees with this view, and it seems reasonable to assume that such is the case. The layer is thick, as Figs. 15 and 16 show, and contains the wavy parallel strands and plates of a dense material that are found in the undoubted reflectors of the Euphausidæ and squids, as well as in the light-organs of many other organisms. A single series of pear-shaped or wedge-shaped nuclei appear in the middle level of this layer with their apices pointing outward (*R. N.*). The remarkable form of these nuclei cannot be explained, and in the other similar reflectors we find, usually, no nuclei at all. In the organ under discussion they form a graduated series, with the

larger ones in the centre and the smaller ones out toward the edge. From what we can see we must designate them as the nuclei of the reflector (*R. N.*).

Behind the reflector is found a mass of ordinary connective tissue (*Conn. T.*) weakly differentiated and organized with relation to the organ, but not taking any specific part, other than an apparently mechanical one, in its organization.

The two luminous species of *Acanthephyra*, *A. pellucida* and *A. debilis*, possess light-organs that show a considerable resemblance to those of *Sergestes*, but which differ from them in many details. They also differ in structure among themselves. Kemp describes their number and position in *Acanthephyra debilis* as follows: "The most highly developed organs in *Acanthephyra debilis* are not all of similar structure as they are in the case of *Sergestes*, but exist in different degrees of complexity in different parts of the animal." "The most highly developed organs are twelve in number, and each is so placed that the light which it produces is thrown directly downwards. One is situated on the distal and external aspect of the protopodite of each pleopod, and one behind the protopodite of each uropod."

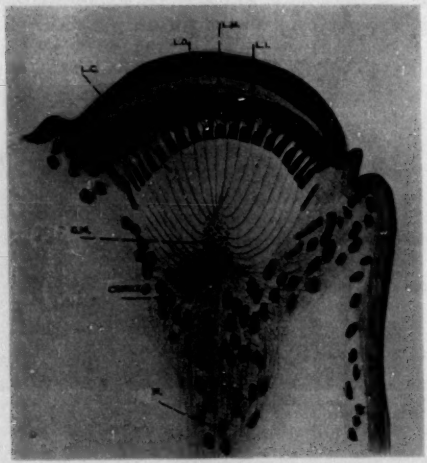
Fig. 17 is copied from Kemp's photograph of this organ. Here we see that a lens is formed, as in *Sergestes*, from the cuticle. This lens (*L. O.*, *L. M.*, and *L. I.*) is not so thick as in *Sergestes*, and its outer surface is convex, while the inner is concave. It shows three layers instead of two, and the extra layer is a middle one. The lens measures 0.24 mm. in diameter, and its entire substance is permeated with a transparent, violet-blue pigment. The middle layer (*L. M.*) does not appear to extend into the general cuticle from which the lens is formed. At the edge of the lens the cuticle is much thinner than even the surrounding general cuticle, and is thrown into folds. This would permit of some movement of the organ as a whole if muscle apparatus is placed in a position to move it.

Inside of the lens appears the same layer of elongate cells that we find in *Sergestes*. They are much longer than in that animal and appear to radiate from a proximal centre. Their inner ends are filled with the same homogeneous and hyaline cytoplasm, and here again the writer must differ with Kemp, who implies that they form a secondary lens, by assuming that they are the gland-cells (*L. C.*) of the organ and that they secrete luciferine. The

nuclei are placed in the extreme distal tips of the cytoplasm, and, as the cells are hypodermal in origin and lie directly against the lens, they must secrete the lens as well as furnish the light. This double function may explain their peculiar structures.

The well-developed reflector of *Sergestes* is represented here by a loose, fibrous mass whose strands radiate in a proximal direc-

FIG. 17.



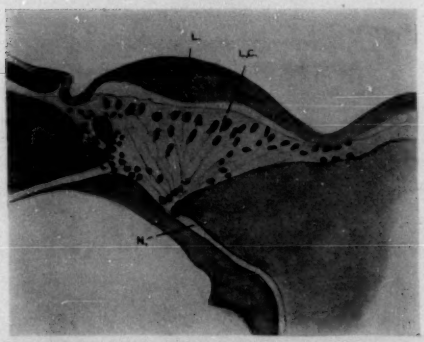

Median vertical section of one of the large light-organs of *Acanthephyra debilis*. *l.o.*, outer layer lens; *l.m.*, middle layer of lens; *l.i.*, inner layer of lens; *l.c.*, light-cells with distal nuclei and long proximal bodies; *g.m.*, granular mass; *conn. t.*, connective tissue; *n.*, nerve. (After Kemp.)

tion from the central point of the light-layer, where they are mingled with a mass of granular matter (*G. M.*). The nuclei that support this structure are placed in masses in an extreme proximal position. We will assume that this arrangement represents an imperfect reflector to some degree, but we must also take account of a nerve-bundle (*N.*) that approaches the photophore from its inner end and distributes its nerve-fibres through the mass of apparent connective tissues (*Conn. T.*). No suitable

methods have been applied to distinguish these nerve-fibres from the connective tissues or to see how and where they end.

This organ is quite evidently a more primitive type of the organs found on *Sergestes*. But in addition to these principal organs in *Acanthephyra* we find even simpler ones (Fig. 18). A good example of such is seen in the freshly-caught specimen as a dark-violet blue streak on each side of the inner wall of the carapace just behind the last pair of thoracic legs. When this streak of blue tissue is cut in transverse section we find that the

FIG. 18.




Transverse vertical section of the long light-organ on side of *Acanthephyra debilis*. *l.*, lens; *l.c.*, light-cells; *n.*, nerve. (After Kemp.)

color is due to a long, cylindrical lens (*L.*) that has been formed by a slight thickening of the cuticle. This lens region is tinged throughout with the blue pigment that gives the organ its external color, and it also shows a weak division into an outer and inner layer, and it has acquired the usual transparency of lens organs. It is still, however, a very weakly developed organ and cannot do much towards focussing the light.

Beneath the cuticular lens is found the usual row or layer of elongate hypodermal cells. In this case, however, they have not developed to the same extent as in the larger organs on the same animal. The nuclei of these cells do not occupy the extreme distal tips of their respective cells, but they show a strong tendency

to do so. Fig. 18 shows this, as it also shows the weak differentiation of a mass of connective-tissue cells below into an indefinite structure that in the more advanced organs becomes a reflector. Traces of a nerve supply (*N.*) are also present, according to Kemp.

In the species of *Hoplophorus grimaldi* the light-organs seem to agree very closely in structure and distribution with those just described in *Acanthephyra*. In regard to the pigmentation of the animals whose photophores have been described above, and to the meaning of these organs, we cannot do better than quote the remarks of Kemp in his excellent paper, as follows:

THE PIGMENTATION OF THE PHOTOPHORES.

"It has already been mentioned that a deep-blue pigment is, in life, associated with the photophores of Decapoda, occurring in *Sergestes* in the first cellular layer and in *Acanthephyra* in the lens itself.

"There is reason to believe that this pigment is closely allied to, if not identical with, that found in the lobster. When the photophore is placed in absolute alcohol the blue color soon becomes bright red, and the same reaction instantaneously appears when it is boiled in a drop of water. If the lens of the Acanthephyra be dissected out and treated with strong sulphuric or nitric acid the color at once changes to red, and immediately afterwards turns to a dull greenish blue of a much less distinct color than that originally present. The greenish-blue tone appears to fade away a little later, but the concluding stages of the reaction are somewhat obscured, owing to the burning of the tissue by the acid.

"The red pigment which gives the familiar coloring to *Nephrops* and to the lobster, when boiled, is known to be one of the lipochromes or fatty pigments, called by Moseley *crustaceorubin*, associated with a small quantity of yellow pigment, known as *Hepatochrome,* which appears to be derived from the liver. The investigations of Krukenberg and of Miss Newbigin seem to show that the unstable blue-black pigment or *lipochromogen* which occurs in the lobster is a compound of the red lipochrome with a complex organic base. The blue color is turned red by any reagent which alters the form of the proteid, and the red pigment, extracted and dried, gives, with strong acids, a brilliant but evanescent blue reaction.

"The photophores are, unfortunately, so minute that it is not possible to extract a solution of the pigment; but the reaction mentioned above, which was obtained by the addition of acid to the lens of *Acanthephyra*, furnishes fairly satisfactory evidence of the nature of the pigment. The following observations on the red coloring-matter of *Acanthephyra* may be mentioned here: An ether extract of the pigment gave a bright-yellow solution, which on evaporation yielded an oily red extract. On the addition of strong nitric acid a bright, but rapidly evanescent, blue reaction was obtained, which was followed by the separation of the red matter from the oily yellow pigment, the latter turning a dull green. This result is practically identical with that obtained by Miss Newbigin with the extracted pigments of *Nephrops*. The red coloring, which turns blue under the influence of the acid, is the lipochrome, *crustaceorubin*, while the oily yellow pigment is *heptochrome*. The acid breaks up the proteid and at once converts the blue *lipochromogen* into the red lipochrome, and this is immediately followed by the characteristic blue reaction which this pigment gives in the presence of an acid. The tissues burn and become brown under the influence of the reagent, and the rapid evanescence of the blue tint, which is characteristic in the case of dry extracted pigment, is in consequence, somewhat masked.

"It has not been possible to test the blue pigment in the photophores of *Sergestes* as fully as has been done in the case of *Acanthephyra*, but from the fact that it turns red when boiled or when treated with strong acids it is very probable that it is of the same nature.

"The existence of blue coloration in deep-sea animals is exceedingly rare, and its occurrence among Decapoda in close association with the photophores is almost unique, for among the Euphausiacea a similar pigment appears to have been noticed only on a single occasion. In November, 1909, a large specimen of *Thysanopoda acutifrons*, Holt and Tatterstall, was caught in a mid-water net off the west coast of Ireland. This specimen, which was dead by the time it reached the deck, was found to possess patches of deep-blue pigment associated with the photophores on the eye-stalks. Casual examination failed to reveal this pigment in the other photophores, which, however, were of a darker color than is usually the case. The specimen was put aside in a dish of water, and when it was again examined, not more than half an

hour later, all trace of the blue pigment had vanished. It is evident that, even if in this case the blue coloring invariably occurs in the photophores, the phenomenon is one of great rarity among Euphausians, for it certainly is not found in *Meganyctiphanes norvegica* or in any of the common North Atlantic species.

"The blue pigment of the photophores of Decapoda is much more stable than that noticed in *T. acutifrons*. Although rapidly extracted by alcohol, it will persist for years in specimens preserved in weak formalin, remaining distinct long after the general red coloring has disappeared.

"The lens of *Acanthephyra*, being blue, can necessarily only allow the emission of blue light, and it is not impossible that this is also true in the case of *Sergestes*, where the lens is transparent and the first cellular layer blue. It seems then that, at least in the former genus, the production of blue light is a necessity, but it is impossible to suggest any explanation of this curious phenomenon.

"Photophores have evidently been developed by crustacea in at least three separate instances. Those possessed by *Acanthephyra* and *Hoplophorus* are in structure wholly distinct from those of *Sergestes*, while in neither case is there any resemblance to the very complex organs of the Euphausiacea.

"It is a remarkable fact that, whereas in the latter order the possession of photophores in the general rule (only in *Bentheuphausia* are they absent), their occurrence in large genera, such as *Sergestes* and *Acanthephyra*, is limited to a few species only. This is particularly noteworthy in *Sergestes*, in which two forms, both of which are classed among a small group of extremely closely allied species, exhibit a large number of photophores, whereas none are to be found in the other members composing the group.

Döflein, in a short but interesting paper, has summarized the various suggestions which have been made as to the use of luminous organs to marine animals. He remarks that they probably serve different functions in different groups of animals, and classes them in four sections:

"I. Attraction of prey (chiefly important in sessile or slowly moving animals).

"II. Attraction of other individuals of the same species, either (*a*) for the formation and maintenance of swarms or (*b*) to

enable the sexes to find and recognize one another. In this connection Döflein points out that animals with a complicated system of photophores always possess highly developed eyes, and refers to Brauer's theory that the varying arrangement of photophores produces light patterns serving as recognition marks, like the color-patterns of animals living in daylight.

"III. Protection. The clouds of luminous secretion emitted by some species may possibly serve the same purpose as the ink of the cuttlefish, and photophores may also, by a sudden flash of light, scare a pursuer. In the fauna of land and shallow water a brilliant coloring is often assumed as a signal that the species is distasteful, and some deep-sea animals may, for the same purpose, exhibit warning lights.

"IV. Illumination of objects viewed by the animal. On this theory it is difficult to account for the ventral and lateral position of the photophores in many marine animals. In Crustacea this is particularly well shown, for the large majority of the organs illuminate regions which seem altogether out of range of the eyesight.

"It is evident that these suggestions will not account for every case which can be found; the photophores in the roof of the branchial chamber of *Sergestes* remain inexplicable.

"The vast majority of marine animals which possess photophores live at the surface or at intermediate depths and never occur on the bottom. No exceptions to this rule have been noticed in the deep-water fauna of the Irish Atlantic slope, but it seems that the two Euphausians, *Meganyctiphanes norvegica* and *Nyctiphanes couchii*, are sometimes found on the bottom in shallow water. On one or two occasions large numbers of these two species have been caught off the Irish coast at depths of forty to sixty fathoms, and there are indications that the specimens which were obtained in these hauls were actually living on the sea-floor. The same two species are frequently obtained over depths of 400 to 800 fathoms off the west coast of Ireland, and here they invariably occur in midwater.

"It must be remembered that the ordinary open-mouthed nets, which are generally employed for bottom work, frequently catch midwater organisms while being hauled, and there is reason to believe that errors arising from this source exist in many of the instances in which animals bearing photophores have been recorded from the bottom.

"Many of the higher marine animals live on the sea-floor at depths to which no ray of sunlight can ever penetrate, and, though they possess well-developed eyes, are themselves, for the most part, without any special illuminating apparatus. That light exists at these depths seems almost certain. It is probably fairly plentiful in regions thickly populated by Cœlenterates, and the excretions of numerous animals of a more highly organized nature have been found to be brilliantly phosphorescent. The restriction of photophores to species living in midwater seems only explicable on the theory that there is a comparatively plentiful supply of light on the bottom itself."

There are other kinds of Crustacea that also produce light. Unfortunately we have but meagre descriptions. Two of the most interesting of these are the large spider crab, *Colossendeis gigas*, and the shrimp, *Pentacheles phosphorus*, both of which were dredged from the depths of the Indian Ocean by Alcock on the research ship *Investigator*.

The spider crab, which was very large, showed a greenish-blue light radiating from the ventral surface of all of its legs. The shrimp show two points of light glowing with a steady radiance from each side of the openings of the oviducts. In daylight these points could be seen as glandular patches of a greasy texture. We have no further information on this subject.

(*To be continued*)

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**Potash in Lake Muds of Western Utah.** ANON. (*U. S. Geological Survey Press Bulletin* No. 271, May, 1916.)—Potash in surprisingly large proportions is present in the brines and muds of the Salduro Marsh, a sink in the Salt Lake Desert, about 60 miles west of the southwest edge of Great Salt Lake. From the clays underlying the salt body which covers the marsh the United States Geological Survey collected samples at depths of 8 to 12 feet, in which the dissolved salts were found to contain from 2 to about 3½ per cent. of potash, and 2¼ per cent. was found in the soluble salts at a depth of about 4 feet. Of the dissolved salts contained in the brines occupying the spaces between the salt crystals in the crust overlying these muds 3 to 4 per cent. was found to be potash.

Singularly enough, the salt crust left at the surface of the desert through the evaporation of the brines contains little more than a trace of potash, most of the potash being confined to the brines and to the muds underlying the salt crust. The successful extraction of this potash is a fascinating as well as most pressing problem for the chemical engineer. According to analyses made by the Survey,

the brines and muds from the Salduro Marsh contain considerable magnesium chloride, as well as chlorides of potassium and sodium, and so are somewhat similar in composition to the deposits from which potash is manufactured in Germany. Therefore, it appears that success in methods for manufacturing potash at the Salduro Marsh should prove comparatively easy. While no extensive exploratory work has been done by the Survey to show the area of the deposit, it is believed that the amount of potash present in the region, if it can be extracted with commercial success, is sufficient to provide a valuable source of supply to the country.

**The Origin of Lightning.** ANON. (*Electrical Review*, vol. 68, No. 20, May 13, 1916.)—Various theories have been presented from time to time to account for the electrical charges which are accumulated by clouds, many of which have been widely discussed. Lightning phenomena are usually accompanied by heavy downpours of rain. It is well understood how the voltage of a cloud may be raised by the combination of many fine charged particles of moisture into drops which are large enough to be precipitated to the earth. The large drop carries the combined charges of all the small drops which go to make it up, but its surface is very much less than the combined surfaces of the component droplets; hence the surface density of the electrical charge is very much greater. When the drop is large enough to fall and approaches the earth, the voltage may be high enough to cause an electrical discharge across the intervening space. But how are the original charges upon the tiny moisture particles produced?

The most plausible explanation for this has been advanced by Dr. George Simpson, who proved that when drops of water are broken up they become charged positively, while the surrounding air receives a negative charge. A thunder cloud is known to form in a rapidly ascending current of air, and if the velocity is as great as 26 feet per second, the smaller drops will be carried upward, while even the largest drops will be unable to progress against the current. The larger drops break up in the air and become electrified, according to Doctor Simpson. If the ascending current spreads out laterally near the top of the cloud, the vertical velocity is diminished, the drops will grow and fall, but only to break again and repeat the process. Sufficient electricity might be thus accumulated to account for the observed effects.

The rain which reaches the earth is sometimes charged positively and sometimes negatively, but more often positively, which is in accord with the above idea. This does not account for the fact that the earth as a whole is negatively charged, although local portions are at times positively electrified. There is still a great deal to be learned in connection with atmospheric electricity, but Doctor Simpson's hypothesis seems to offer an adequate explanation for the existence of thunder clouds and to be free from objections of a theoretical nature.

## NOTES FROM THE U. S. BUREAU OF STANDARDS.*

### PLASTIC FLOW.[1]

By Eugene C. Bingham.

EXPERIMENTS by Bingham and Durham[2] showed that the fluidity of a suspension is a linear function of the concentration. The zero of fluidity is reached at a comparatively low volume-concentration, as is shown in Fig. 1. The concentration which has zero fluidity serves to sharply demarcate viscous from plastic flow. All concentrations of solid less than this are viscous, and any shearing force—no matter how small—will produce permanent deformation, if long enough exerted. Concentrations greater than this are plastic, and it is necessary to use a shearing force of finite magnitude in order to produce a permanent deformation. The laws of plastic flow have never been studied.

The method of attack was to force suspensions of clay and water, under known pressure, through capillaries of different dimensions, and to measure the rate of flow. Some of the values obtained are shown in Fig. 2. For medium pressures the volume of flow per second is given by the formula

$$v = K\ (P - f)$$

where $P$ is the pressure employed and $f$ is the so-called "friction"; *i.e.*, the force required to start the flow.

Putting $P - f$ in place of $P$ in the ordinary Poiseuille formula for calculating the fluidity, we have a means for calculating the "mobility" of plastic substances, analogous to the fluidity of viscous substances.

The friction increases as a linear function of the concentration of solid present (see Fig. 1). It is independent of the length and diameter of the capillary as well as the viscosity of the medium. It is, however, affected by the presence of alkalies or acids in the medium.

* Communicated by the Director.

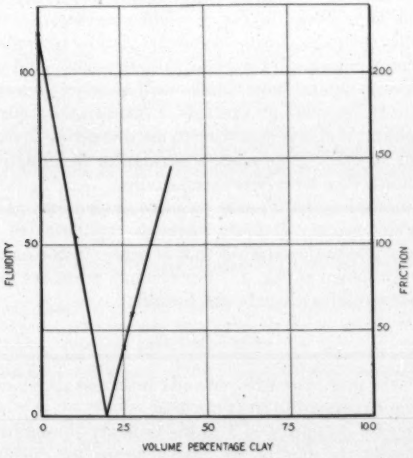
[1] Scientific Paper No. 278.

[2] *Am. Chem. Journal*, **46**, 278 (1911).

The mobility decreases rapidly as the concentration of solid is increased, as is seen in Fig. 3. The mobility is also enormously sensitive to the presence of alkalies or acids, the mobility of a 50 per cent. by weight clay suspension being increased 330 per cent. by the addition of 0.1 per cent. of potassium carbonate.

At pressures little if any greater than those necessary to overcome the friction there was detected seepage of the medium past the solid particles (see Capillary 6.1 Fig. 2). At high pressures

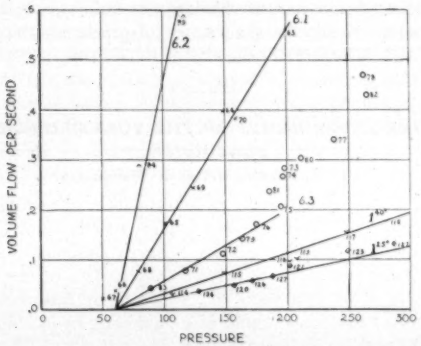
FIG. 1.




there was sometimes a sudden increase in the rate of flow, which is apparently due to slipping (see Capillary 6.3, Fig. 2).

If the solid material consisted of spheres of equal size, the pore space remaining when the particles were as closely packed as possible would amount to 26 per cent., and quite irrespective of the radius of the spheres. However, due to the friction of the spheres on each other, the pore space may be much larger than this, and this is particularly true if the material is very finely divided. As a matter of fact, it was found that on shaking dry clay into a flask, the pore space remaining amounted to 81.6 per cent. of the

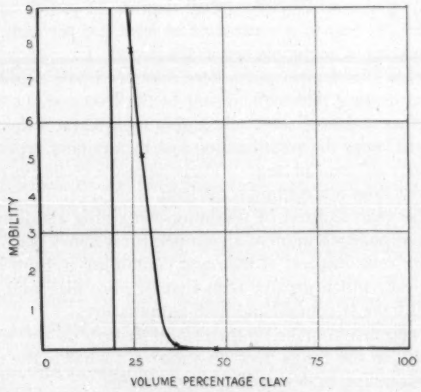
FIG. 2.




The flow (in c.c.) of 50 per cent. clay suspension in water containing 0.1 per cent. of potassium carbonate in solution, for pressures (g. per sq. cm.) as shown, and at 25° C., except one series of experiments with Capillary No. 1, which was made at 40° C. The capillaries had the following dimensions:

| Capillary | Radius in cm. | Length in cm. |
|---|---|---|
| 1 | 0.02848 | 2.468 |
| 6.1 | 0.05785 | 5.071 |
| 6.2 | 0.05811 | 2.509 |
| 6.3 | 0.05850 | 9.998 |

FIG. 3.



total volume. This corresponds closely to the percentage of liquid present in the mixture having zero fluidity, which is 80.5. It is upon this friction that the plasticity depends, and the plasticity is thus closely related to the fineness of subdivision of the material.

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## FURTHER EXPERIMENTS ON THE VOLATILIZATION OF PLATINUM.*

By G. K. Burgess and R. G. Waltenberg.

THIS is a continuation of an investigation undertaken at the suggestion of the Committee on "Quality of Platinum Utensils" of the American Chemical Society. Seven platinum crucibles of various makes and purity have been subjected to successive heatings at 700, 1000, and 1200° C., followed by determination of iron and other materials soluble in 1 : 4 boiling hydrochloric acid. Among the results obtained are the following:

1. Platinum ware in the form of crucibles of whatever degree of purity behaves, with respect to gain or loss of weight, on heating in air at ordinary atmospheric pressure, in a manner characteristic only of the temperature of heating.

2. Each impurity, as iridium, rhodium, or iron, appears to exert its effect on the volatilization of platinum independently.

3. For platinum crucibles of all degrees of purity containing Ir, Rh, Fe, Si (up to a content of at least 3.0 per cent. Ir) the loss on heating is negligible below about 900° C.

4. Below this temperature there may even be a slight gain in weight on heating platinum, owing to the iron content diffusing to the surface and oxidizing. At higher temperatures the presence of iron will lower the volatilization loss by amounts depending on the quantity of iron present. There appears to be no platinum made which does not contain some iron.

5. The volatilization of platinum containing rhodium is less than that of pure platinum at all temperatures above 900° C.

6. The volatilization of platinum containing iridium is, above 900° C., very much greater than that of pure platinum, and increases with the Ir content and with temperature.

7. It appears to make no material difference in the volatilization results, in the range 700° to 1200° C., what is the order of heating, ascending or descending temperatures.

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* Scientific Paper No. 280.

8. In an oxidizing atmosphere at temperatures of the order of 1000° C. platinum, in the presence of, but not in contact with, silica, will apparently take up small quantities of this substance.

9. The loss in crucible weight due to the solution of soluble matter in HCl, after heating, is variable, depending on the crucible, and may be large. This loss is relatively greater at low than at high temperatures.

10. All of the above losses, caused by heating, acid treatment, and iron diffusion, apparently continue with undiminished magnitude after the first treatment, which is usually erratic.

11. The following table gives the approximate changes in weight to be expected for heating platinum containing iridium or rhodium, but nearly free from iron. The presence of iron in appreciable quantities renders the prediction uncertain, but it always acts in the direction of lowering the volatilization loss. Silica, if taken up from the furnace, will also tend to lower the results slightly.

Approximate loss in mg./100 cm.²/hour at temperatures indicated for platinum nearly free from iron.

| Platinum containing | Pure Pt | 1 per cent. Ir | 2.5 per cent Ir | 8 per cent. Rh |
|---|---|---|---|---|
| 900 or less | 0 | 0 | 0 | 0 |
| 1000 | 0.08 | 0.30 | 0.57 | 0.07 |
| 1200 | 0.81 | 1.2 | 2.5 | 0.54 |

## DISTRIBUTION OF ENERGY IN THE VISIBLE SPECTRUM OF AN ACETYLENE FLAME.*

By W. W. Coblentz and W. B. Emerson.

Data on the distribution of energy in the visible spectrum of a standard source of light are frequently needed in connection with investigations in physiology, in psychology, and in physics; especially in photo-electric work, in photography, and in the photometry of faint light sources. Frequent requests for such data have come to this Bureau. The acetylene flame appears to be a promising source of light, having a high intensity and a white color. The present paper gives data on the distribution of energy in the visible spectrum of a cylindrical acetylene flame, operated under specified conditions.

* Scientific Paper No. 279.

In the region of the spectrum extending from the yellow to the violet, the spectral energy distribution of all the flames examined appears to be the same, within the limits of observation. On the other hand, in the region of the spectrum extending from the red toward the long wave-lengths the emissivity is greatly affected by variation in thickness of the radiating layer of incandescent particles in the flame. Hence in and beyond the red part of the spectrum the data apply only to cylindrical flames which are operated under specified conditions.

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## FURTHER DATA ON THE OXIDATION OF AUTOMOBILE CYLINDER OILS.*

**By C. E. Waters.**

IN continuation of work already published by the Bureau of Standards, as well as in the *Journal of Industrial and Engineering Chemistry*, a study was made of the rate of oxidation of three automobile cylinder oils when exposed to sunlight and air. This was done by determining the increase in weight and in acidity at intervals during a period of 438 hours' exposure. The accompanying changes in the carbonization values were also determined. The general result was that there is a gradual lessening of the rate at which the weight increases, and at the same time the formation of acid and the carbonization value increase more and more rapidly.

The Maumene numbers of the oils increased greatly as a result of oxidation, while there was a marked drop in the iodine numbers. After oxidation the oils showed a much greater tendency than before to emulsify when agitated with water. Filtration through animal charcoal removed, to a certain extent, the substances that caused this tendency, and that raised the carbonization values.

When the three oils used in the work above, and eight others, were heated to 250° C. for periods ranging from one to seven hours, the formation of carbonized matter proceeded at a rapidly increasing rate. The same was true of the eleven oils when heated for three hours at various temperatures from 230° to 280° C. It was found that in both cases the greater the carbonization value at first, the more rapidly did it increase as the tempera-

* Technologic Paper No. 73.

ture was raised or the time of heating extended. In other words, an oil which had a low carbonization value if heated to 250° for two or three hours, and an oil showing a somewhat higher value under the same conditions, will be further and further apart as the conditions become more strenuous. This being so, it is unnecessary to greatly prolong the time of heating in routine testing.

The need of extreme care in taking and preserving samples, as well as in testing them, was emphasized, because the presence of rust particles or other extraneous matter increases the amount of carbonization.

In conclusion it is shown that the carbonization value is independent of the flash- and fire-points and of the evaporation loss on heating.

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## AN INTERLABORATORY PHOTOMETRIC COMPARISON OF GLASS SCREENS AND OF TUNGSTEN LAMPS, INVOLVING COLOR DIFFERENCES.*

By G. W. Middlekauff and J. F. Skogland.

IN 1911 the Bureau of Standards and the National Physical Laboratory of England, in coöperation, established groups of 1.5-wpc. tungsten standards, using Lummer-Brodhun contrast photometers in stepping from corresponding groups of 4-wpc. carbon standards. Although the agreement between the two laboratories was very satisfactory and subsequent measurements of the new standards at the Bureau checked the original values, it was realized, in view of the small number of observers in each laboratory, that if other groups of observers had made the measurements or if some other photometric method had been used the results *might* have been different.

Therefore, in order to obtain information as to the agreement which might be reasonably expected among different groups of experienced observers working by the same and by different methods, the Bureau invited the Nela Research Laboratory, the Electrical Testing Laboratories, and the Physical Laboratory of the United Gas Improvement Company to coöperate in an intercomparison of photometric measurements of blue-glass screens and tungsten lamps involving color differences such as

* Scientific Paper No. 277.

were encountered in the establishment of the new standards. The first two laboratories, like the Bureau, used Lummer-Brodhun contrast photometers, while the third used a special flicker photometer, and in no laboratory were the screens and lamps measured at the same time.

The results of the intercomparison show that each observer, regardless of the kind of photometer used, maintained a fairly definite criterion with respect to the mean of his laboratory, and that each laboratory likewise consistently maintained its relation to the mean of all, as judged from the measurements on the screens and those made on the lamps some months afterwards.

Considering the difficulties involved in the measurements, the different characteristics of observers, and the wide difference in illumination employed, the agreement among the laboratories was remarkably good. It is true, however, that although the differences are small they are not negligible in precision photometry. It is evident, therefore, that measurements to establish standards involving color difference should be left as much as possible to the standardizing laboratory, where the observers must be carefully selected and a considerable number employed, and the kinds of instruments and other conditions definitely fixed.

An examination of the Bureau's observers who took part in this intercomparison and who were included in a group of 114 observers tested at the Bureau by Crittenden and Richtmyer, using a special flicker photometer, shows that their mean characteristic is very approximately the same as that of the average of the 114.

Furthermore, the flicker values found in this intercomparison and also by Crittenden and Richtmyer for the tungsten lamps at 1.5 wpc. are in agreement with the Bureau's values. Hence it is concluded that the values which were originally assigned to the new 1.5-wpc. tungsten standards as a result of the intercomparison with the National Physical Laboratory can be considered as average eye values.

## NOTES FROM NELA RESEARCH LABORATORY.*

### NOTES ON FLICKER PHOTOMETRY: FLICKER-PHOTOMETER FREQUENCY AS A FUNCTION OF THE COLOR OF THE STANDARD, AND OF THE MEASURED, LIGHT.

By Leonard T. Troland.

THE *flicker-photometer frequency* of any two visual stimuli may be defined as the rate of alternation (cycles per second, with equal intervals) of the two in the same photometric field, which is just sufficiently rapid to eliminate flicker, when the ratio of their intensities is such as to give a minimum of flicker at a slightly lower rate.

The measurements recorded below were made with an instrument of the Whitman disk type, operated by an adjustable speed synchronous motor. The field was an annulus, of 0.23 degrees internal and 1.14 degrees external diameter, so that stimulation was strictly foveal. This was viewed in dark surroundings, and each setting was made after approximately 30 seconds' fixation of the central dark area, thus insuring fairly stable local adaptation. The artificial pupil employed was a square, 2.51 mm. on a side. Care was taken to reduce scattered light in the spectrometer system to a minimum.

Two series of measurements were taken with sixteen spectral colors, and a " physiological white " standard, of constant intensity for each series. This standard consisted of tungsten light corrected with a blue glass, so as to exhibit no chromatic tinge either when viewed directly or in the after-image reaction produced by dimming the light upon a retinal area already strongly " fatigued " by it (Hering's test for a physiological white). All of the spectral colors were equated in brightness to the standard, by the criterion of flicker, as a part of each measurement. The results for the two intensities of 1025 and 547 photons,[1] respectively, are given in the first two columns of the table below.

* Communicated by the Director.

[1] One *photon* is an illumination of the retina corresponding with a stimulus-surface brightness of one candle per square metre, and an effective pupillary area of one square millimetre.

| Color | Wave-length in μμ | Flicker-photometer frequency cycles per second | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | White standard | | | | Plain tungsten standard, 510 photons A.D. | | Over-corrected tungsten standard, 510 photons A.D. | |
| | | 1025 photons A.D. | | 547 photons A.D. | | | | | |
| Red | 648.2–720.0 | 27.76 | .18 | 24.69 | .26 | ..... | ... | ..... | ... |
| Red | 693.9–720.0 | ..... | ... | ..... | ... | 23.57 | .05 | 24.63 | .14 |
| Red | 676.4–700.0 | 28.15 | .08 | 24.79 | .17 | 23.82 | .14 | 24.04 | .20 |
| Red | 658.6–680.0 | 27.93 | .14 | 24.34 | .09 | 23.88 | .11 | 23.83 | .26 |
| Red-orange | 640.7–660.0 | 27.54 | .09 | 23.86 | .05 | 23.22 | .10 | 23.60 | .20 |
| Orange | 629.4–640.0 | 26.70 | .10 | 23.62 | .08 | 22.57 | .10 | 23.19 | .23 |
| Orange | 610.4–620.0 | 24.02 | .17 | 22.50 | .26 | 20.68 | .24 | 21.57 | .26 |
| Yellow | 591.5–600.0 | 20.26 | .40 | 19.54 | .09 | 16.14 | .09 | 18.15 | .14 |
| Yellow | 572.3–580.0 | 17.10 | .35 | 15.94 | .15 | 17.34 | .006 | 17.02 | .23 |
| Yellow-green | 553.1–560.0 | 17.82 | .14 | 17.83 | .10 | 18.33 | .24 | 16.51 | .32 |
| Yellow-green | 533.8–540.0 | 19.07 | .26 | 18.30 | .05 | 18.03 | .08 | 17.66 | .18 |
| Green | 514.5–520.0 | 21.79 | .18 | 18.86 | .15 | 19.90 | .20 | 18.67 | .10 |
| Blue-green | 492.1–500.0 | 22.49 | .29 | 21.98 | .15 | 21.94 | .10 | 21.93 | .21 |
| Blue | 473.1–480.0 | 25.26 | .14 | 22.46 | .26 | 23.18 | .17 | 23.00 | .06 |
| Blue | 444.0–460.0 | 26.13 | .07 | 23.12 | .12 | 24.22 | .11 | 23.88 | .13 |
| Violet | 426.7–440.0 | 25.76 | .15 | 22.99 | .07 | 23.61 | .04 | 23.53 | .10 |
| Violet | 408.1–420.0 | 24.13 | .19 | 21.73 | .44 | 22.61 | .21 | 22.02 | .11 |

As will be seen from the table, the flicker-photometer frequency for a white standard varies radically with the spectral character of the measured light, being greater at the ends of the spectrum than in the middle, with a minimum at about 575μμ. Similar results appear in the rougher data of Ives, who used uncorrected "carbon" light. In order to test the hypothesis that the position of the minimum was determined by a subliminal chromatic factor in the standard, very careful comparative measurements were made with two standards of equal brightness—510 photons—but of different color, one being plain tungsten light at low efficiency (having a definite orange tinge) and the other being an over-corrected tungsten light (decidedly bluish, and of about the same saturation as the plain tungsten). The results are shown in the third and fourth columns of the table. They prove that the flicker-photometer frequency is determined primarily by the character of the spectral stimuli, in relation to white, although a marked color tone in the standard will shift the position of the minimum.

Each value in the first two columns represents 4 independent determinations, except in a few cases, where 8 were taken. The values in the third column are averages of at least 10 determinations, and those in the fourth column of at least 15 determinations, in each case. The deviation measures are those of the averages.

No influence of the color of the standard upon the intensity required for a match was apparent within the limits of reliability of the measurements. The photometric sensibility, however, was found to depend on the color of the standard, and also on that of the measured light. The sensibility was exceedingly low in the red, as shown by the following table:

| Color | Wave-length | Average percentage deviation in photometric brightness for a match | |
|---|---|---|---|
| | | Plain tungsten standard | Bluish standard |
| Red ..... | 693.9–720.0 | 4.45 | 6.39 |
| Orange-Red ... | 640.7–660.0 | 4.43 | 6.70 |
| Yellow ..... | 572.3–580.0 | 0.89 | 1.83 |
| Blue-Green .... | 492.1–500.0 | 1.65 | 2.05 |
| Violet ..... | 408.1–420.0 | 0.99 | 2.07 |

All of the above results are for the writer's right eye. The investigation is being continued, and a more detailed description of the conditions will be given in a later, extended account.

Nela Research Laboratory,
National Lamp Works of General Electric Company,
Nela Park, Cleveland, Ohio,
May 18, 1916.

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## THE LAWS OF VISUAL MINUTHESIS: THE INFLUENCE OF INTENSITY ON THE EQUALITY TIME-FUNCTION.

By Leonard T. Troland.

THE time, $t_q$, required for a fresh negative after-image, projected on a reacting field of light, to just fall below the threshold may be called the *equality-time*, since it is the time needed for two differentially minuthetized ("fatigued") retinal areas to reach sensibly equal degrees of adaptation. The after-image must be produced by preëxposure of the eye to a primary stimulus during an interval $t_p$, the preëxposure-time, which immediately precedes the interval $t_q$. The function, $t_q = f(t_p)$, may be called the *equality-time function*, which is shown by experiment to be representable by a curve of the saturation type.

Measurements were made to determine the influence of stimulus intensity upon this function, the primary and the reacting lights being of the same color and brightness. The field was circular, with an angular diameter of 3.38 degrees, was provided with a central fixation point, and had dark surroundings. The initial minuthesis was produced by exposure either of the right or

left half of the field, and during the " equality period " the resulting after-image was projected on the full circle so as to occupy its original position on the field. A circular artificial pupil of 2.36 mm. diameter was employed, but the intensities, given in the table, are expressed in *photons; i.e.*, in candles per square metre for an effective pupillary area of one square millimetre. The intensity measurements were made by flicker photometry. Five minutes' dark adaptation was allowed before beginning a series of observations.

I. Results for Red: 673.5–760.0 $\mu\mu$

| Intensity in photons | Equality-time, $t_p$ (in seconds), for a preëxposure-time, $t_p$, of | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 4 seconds | A.D. | 32 seconds | A.D. | 128 seconds | A.D. | 256 seconds | A.D. |
| 3.89 | 7.38 | 0.49 | 42.3 | 2.2 | 62.9 | 2.4 | 68.3 | 3.4 |
| 19.45 | 16.1 | 1.0 | 57.4 | 2.2 | 89.1 | 3.5 | 102.2 | 2.6 |
| 97.2 | 10.64 | 0.43 | 54.3 | 2.4 | 93.3 | 2.0 | 124.8 | 4.7 |
| 486.0 | 19.3 | 1.4 | 56.8 | 3.0 | 114.7 | 5.3 | 121.5 | 3.1 |
| 2430.0 | 16.9 | 1.5 | 76.4 | 5.3 | 118.8 | 4.3 | 141.7 | 6.0 |

II. Results for Green: 516.1–525.4 $\mu\mu$

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 3.89 | 11.44 | 0.70 | 42.1 | 3.5 | 73.7 | 2.1 | 77.6 | 3.9 |
| 19.45 | 13.7 | 1.7 | 73.8 | 3.2 | 88.7 | 2.2 | 116.9 | 3.5 |
| 97.2 | 17.38 | 0.63 | 68.3 | 2.7 | 115.5 | 1.4 | 125.4 | 5.0 |
| 486.0 | 16.08 | 0.62 | 64.6 | 2.3 | 104.8 | 2.7 | 122.9 | 4.0 |
| 2430.0 | 18.2 | 2.00 | 52.1 | 2.6 | 106.6 | 3.1 | 121.1 | 4.4 |

Each of the above values is the average of ten independent measurements, and the deviation measures are those of the averages themselves. Each intensity is five times the immediately preceding one, and the highest corresponded to an external brightness of 500 candles per square metre.

An examination of the table shows that above 100 photons the equality-time function is almost independent of the absolute intensity, although there is a general tendency for the value of $t_q$, for a given magnitude of $t_p$, to increase slightly with intensity increase. The table also reveals the relative independence of the function with respect to the color of the stimulus.

The above results are for the author's two eyes, the right and left eyes being employed an equal number of times. A brief series with another subject showed similar relationships.

Nela Research Laboratory,
National Lamp Works of General Electric Company,
Nela Park, Cleveland, Ohio,
May 18, 1916.

## THE THERMAL EXPANSION OF TUNGSTEN AT INCANDESCENT TEMPERATURES.

By A. G. Worthing.

THE measurements of the change in length with temperature were made on straight tungsten filaments of large cross-section. The positions selected on the filaments were sufficiently removed from the lead-in junctions so that their cooling effects were negligible. Using the temperature scale previously reported,[1] the results obtained for the region 1200° K. to 2700° K. are given very closely by the following formula:

$$\frac{L-L_{300}}{L_{300}} = 4.49 \times 10^{-6} (T-300) + 2.4 \times 10^{-12} (T-300)^3,$$

where $L$ represents the length at a temperature $T$ and $L_{300}$ the length at 300° K.

The formula represents also the single value at room temperature (300° K.). The region between room temperature and 1200° K. will be included in the final publication.

Nela Research Laboratory,
National Lamp Works of General Electric Company,
Nela Park, Cleveland, Ohio.

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**Radium Never Seen in Nature.** ANON. (*U. S. Geological Survey Press Bulletin*, No. 267, April, 1916.)—Radium is a metal and is described as having a white metallic lustre. It has been isolated only once or twice, and few people have seen it. Radium is ordinarily obtained from its ores in the form of hydrous sulphate, chloride, or bromide, and it is in the form of these salts that it is usually sold and used. These are all white or nearly white substances, whose appearance is no more remarkable than common salt or baking powder. Radium is found in Nature in such exceedingly small quantities that it is never visible even when the material is examined with a microscope. Ordinarily radium ore carries only a small fraction of a grain per ton of material, and radium will never be found in large quantity, because it is formed by the decay of uranium, a process which is wonderfully slow, and radium itself decays and changes to other elements so rapidly that it is impossible for it to accumulate naturally in visible masses. Minerals that carry radium, however, are fairly easy to determine. One of them, pitchblende, as generally found, is a black mineral about as heavy as ordinary iron, but much softer. The principal radium mineral, carnotite, has a bright canary-yellow color, and is generally powdery. There are other radium-bearing minerals of less importance.

[1] JOURNAL OF THE FRANKLIN INSTITUTE, 181, p. 417, 1916; *Phys. Rev.*, ii, 7, p. 497, 1916.

**Centennial of the Coast Survey.** ANON. (*Scientific American*, vol. cxiv, No. 17, April 22, 1916.)—Those who are inclined to think that the broad and valuable scientific work carried on at Washington under the auspices of the National Government is a modern development will be interested to learn that the United States Coast Geodetic Survey celebrated, on April 5 and 6, the centennial of its establishment. Even in the early days of the nineteenth century, when the shore line of the United States was far less than to-day, the importance of an accurate knowledge of the coast was appreciated, and accordingly Congress, in 1807, authorized the establishment of a National Coast Survey. A plan was submitted by Ferdinand B. Hassler, a Swiss engineer who had emigrated to the United States in 1805 and had been acting professor of mathematics at the United States Military Academy and professor at Union College. This plan was not put into effect until 1811, and actual field work was not begun until 1816. Unfortunately, the importance of surveying newly-acquired territory on state lines and fixing boundaries by permanent marks, after these positions had been determined astronomically, has not always been realized. Frequently difficulties would have been avoided, the settlement of which involved a financial outlay far greater than would have been required for the adequate support of the Coast Survey.

The actual geographic work of the United States Coast Survey is based on a system of main and secondary triangulation which covers the entire United States. On the Atlantic Seaboard the Survey has carried out a complete scheme of primary triangulation, while a second extensive system of triangulation extends across the continent along the 39th parallel of latitude and connects the surveys of the two coasts, furnishing a basis for the surveys of the thirteen states through which it passes. Other triangulation systems have been extended throughout the United States and expanded in various individual states. From the primary and secondary triangulations a tertiary triangulation has been developed along the entire Atlantic and Gulf coasts and Porto Rico, and the Pacific coast, except Alaska, where work is still in progress, as is also the case in the Philippines. The astronomical positions of the various points on the systems of triangulation have been determined by the use of the zenith telescope for latitude and the telegraph for longitude. The familiar charts issued by the United States Government show hydrographic data, including all harbors, channels, buoys, etc., as well as the topography for a few miles inland, and, in the case of rivers and other indentations, to the head of tidewater. Deep-sea soundings are made and tidal records are compiled and published. Terrestrial magnetism is another field in which the operations of the Survey have been carried on, and the study of the force of gravity has been the subject of a number of important investigations. Lines of precise levels cover the United States in a network in which the Coast Survey has coöperated with other government agencies and several railways, and the prosecution of this work is from year to year becoming increasingly important.

## NOTES FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY.*

### THE BRITTLENESS OF ANNEALED COPPER.

By W. E. Ruder.[1]

EXPERIMENTS upon the effect of the more common gases for regular and deoxidized copper showed that the brittleness often developed by heating and frequently ascribed to burning is in reality due to deoxidation. With ordinary commercial copper serious brittleness begins to appear at 400° C. in dry and 600° in wet hydrogen, at 800 to 850° in carbon monoxide, and at 700° in steam. Copper previously deoxidized by the addition of boron remains unaffected at all temperatures in a reducing atmosphere. The brittleness is, therefore, probably due to the reduction of the cuprous oxide around the primary copper grains, leaving a spongy mass with little mechanical strength.

**The Electrical Capacity of Gold-leaf Electroscopes.** T. BARRATT. (*Proceedings of the Physical Society of London,* vol. xxviii, part iii, April 15, 1916.)—The modern gold-leaf electroscope has for some considerable time been employed by workers in radio-activity as an instrument of precision comparable with that of other instruments used in electrical measurements. Many workers in other branches of physics, however, still appear to regard the instrument as merely of historical interest. It is the experience of the author that, with the help of the gold-leaf electroscope, measurement of potential can be made of, at any rate, 1 per cent. between, say, 50 and 300 volts, the limits depending on the particular instrument. The gold-leaf electroscope possesses many advantages over the usual type of electrometer. The latter is exceedingly troublesome to set up and work, and requires very great care in maintaining satisfactory insulation. Its capacity is many times that of the electroscope, which can therefore measure much smaller currents. In addition, the electroscope is much cheaper, takes up very little space, is easily transported, and can be used in any position.

* Communicated by the Director.

[1] *Transactions of the American Electrochemical Society,* vol. 29.

The capacities of gold-leaf electroscopes of various patterns have been determined by a method which depends upon obtaining the relation between the divergence of the leaf and the potential applied to it, and the observation of the fall of potential of the leaf system when it shares its charge a convenient number of times with a standard parallel plate air condenser. It is found that the capacity is practically independent of the amount of divergence of the leaf, except when this divergence is very small, in which case the capacity becomes slightly lower. Ionization currents of the order $10^{-12}$ ampères can be accurately measured by an electroscope of capacity 1 cm. For some purposes the gold-leaf electroscope possesses marked advantages over the quadrant electrometer. The method employed was found to give satisfactory agreement with the results given by another method.

**Delaware Water Gap Cut by Nature's Whip-saw.** ANON. (*U. S. Geological Survey Press Bulletin*, No. 274, May, 1916.)—Delaware Water Gap is a vertical-walled trench, 1200 feet deep, in the narrow ridge of Kittatinny Mountain through which Delaware River flows. Did the river find this gateway ready-made through the mountain or did it cut its way through the hard mountain ledges, and if so, how could it accomplish its mighty task?

By the study of the geology of the region the following history has been worked out. After the rocks had been formed, layer by layer, as sediments in the sea they were folded and tipped on end and worn down by Nature's forces to a gentle surface across which Delaware River flowed to the sea. The top of Kittatinny Range was then part of this surface, and the adjacent area that is now lowlands stood nearly at the same level. Elevation of the land caused the Delaware and its tributaries to wear away the softer rocks and leave the harder rocks standing in relief as ridges. The hard rocks that compose Kittatinny Range formed rapids in the Delaware where it crossed them, but the river gradually cut this barrier away.

It is easy to believe that streams can remove soft shale and limestone in their course, but it may seem at first thought impossible that water alone can cut away hard rock. The water, however, is only a medium, for the cutting is done by the sand, gravel, and bowlders carried by the stream, just as emery fed to a saw cuts through the hardest rock or steel. Large, round holes that were ground into hard rocks by the churning of pebbles at the bottom of small falls have been left as "potholes" on the sides of gorges as the evidence of such stream cutting. So the Delaware, concentrating its power on a small section of the hard rock of Kittatinny Range, was able, during a long period, to cut the gap through the rocky barrier.

The story is told more fully and in plain language in the text printed on the back of the U. S. Geological Survey's Delaware Water Gap map, which is sold by the Survey for 10 cents.

# THE FRANKLIN INSTITUTE

*(Proceedings of the Stated Meeting held Wednesday, May 17, 1916.)*

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, May 17, 1916.

PRESIDENT DR. WALTON CLARK *in the Chair.*

Additions to membership since last report, 5.

The Chairman announced that the business of the meeting would be the annual presentation of the Institute's highest awards in recognition of distinguished scientific and technical achievements, and recognized Dr. Harry F. Keller, who gave an account of the work of Dr. Theodore William Richards, of Harvard University, recently recommended by the Institute's Committee on Science and the Arts for the Franklin Medal in recognition of his "numerous and important contributions to inorganic, physical, and theoretical chemistry, and particularly his classical series of redeterminations of the atomic weights of the more important chemical elements." Dr. Keller then read a letter from Mrs. Richards and a telegram from Dr. Richards regretting that a temporary illness prevented the latter from being present to receive the medal in person. The President announced that the medal and accompanying certificate would be forwarded to Dr. Richards.

Dr. Keller then introduced Dr. John J. Carty, chief engineer of the American Telephone and Telegraph Company, who had also been recommended for the award of the Franklin Medal in recognition of his "long-continued activities in the telephone service, his important and varied contributions to the telephone art, his work in the establishment of the principles of telephone engineering, and his signal success in directing the efforts of a large staff of engineers and scientists to the accomplishment of the telephonic transmission of speech over vast distances."

The Chairman presented the medal to Dr. Carty, who expressed his thanks for the honor conferred upon him and then read his paper on "The Telephone Art."

Dr. Keller was again recognized by the Chairman and described the work of the American Telephone and Telegraph Company, which had been recommended for the award of the Elliott Cresson Medal in recognition of its "constructive and far-seeing policy in the development of the art of telephony, in the promotion of telephone engineering, in the establishment of its telephone system in every part of the United States, and for placing all of the states of the Union in speaking communication." He introduced Mr. Theodore N. Vail, president of the company, to whom the medal was presented. Mr. Vail, in a brief address, expressed his thanks and the thanks of his associates and every individual of the Bell System for the complimentary tribute.

Dr. Hoadley was then called upon to read Dr. Richards's address on

"The Essential Attributes of the Elements," which had been prepared for the occasion.

This was followed by a demonstration of transcontinental and wireless telephony given by the American Telephone and Telegraph Company. Messages were received from and transmitted to numerous western cities, including Pittsburgh, Chicago, Denver, Omaha, Salt Lake City, Winnemucca, and San Francisco. Telephonic communications were received by wire at Arlington, Virginia, then transmitted by wireless to New York City, and from that city by wire to the audience.

Greetings were exchanged by various members of the Institute and nonresident members and others in San Francisco, and musical selections played in the latter city were heard by the entire audience, each chair being supplied with a telephone receiver.

A talking-moving picture of Mr. Thomas A. Watson, early associate of Dr. Alexander Graham Bell, describing the latter's earliest experiments with the telephone, as well as moving pictures of telephone construction and operation, were shown.

Adjourned.

R. B. OWENS,
*Secretary.*

Demonstrations of transcontinental telephony were repeated at 6, 7:15, and 8:30 o'clock P.M., at which Vice-president Louis E. Levy presided. Each demonstration was preceded by an explanatory address by Mr. W. F. Schmidt, of the American Telephone and Telegraph Company.

(A full account of the meeting will appear in the next issue.)

## COMMITTEE ON SCIENCE AND THE ARTS.

(*Abstract of Proceedings of the Stated Meeting held Wednesday, May 3, 1916.*)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, May 3, 1916.

MR. C. E. BONINE *in the Chair.*

The following report was presented for final action:

No. 2667.—Dixie Magneto. Advisory.

The following report was presented for first reading:

No. 2672.—Self-adjusting Pipe Wrench. Advisory.

R. B. OWENS,
*Secretary.*

## SECTIONS.

*Mechanical and Engineering Section.*—A meeting of the Section was held in the Hall of the Institute on Thursday, April 27, 1916, at 8 P.M.

Mr. George R. Henderson, president of the Section, occupied the chair.

Mr. Walter V. Turner, assistant manager, Westinghouse Air Brake Company, Wilmerding, Pa., delivered a lecture, entitled "The Vital Relation

of Train Control to the Value of Steam and Electric Railway Properties." The lecturer, with the help of lantern slides, demonstrated that train control is as potent a factor in the producing value of a railroad as is the locomotive. The fundamental purpose of a railroad is to save time. To avoid duplicating properties, capacity is essential, and this involves high speed and great frequency of trains. Increased capacity by such means is practicable only to the degree that train control is adequate. Safety is as essential to integrity of traffic and successful operation as earning power. Consequently, the relative value of railway properties is entirely dependent upon the ability to keep trains in motion as close together as the state of the art for controlling trains will permit. Railroad capacity in cities has become an exceedingly important consideration, since the transient population during the day, because of "skyscrapers," is very great as compared with that of a few years ago. A brief illustration was given of recent development in train control equipment which has resulted in the doubling of railroad capacity.

After an interesting discussion by Messrs. Young, Gibbs, and others, a rising vote of thanks was extended to Mr. Turner.

Adjourned.

T. R. PARRISH,
*Acting Secretary.*

## MEMBERSHIP NOTES.

### ELECTIONS TO MEMBERSHIP.

(*Stated Meeting, Board of Managers, May 10, 1916.*)

RESIDENT.

MR. THOMAS H. GRIEST, civil engineer, 646 Westview Avenue, Germantown, Philadelphia, Pa.

NON-RESIDENT.

MR. G. M. BASFORD, president, Locomotive Feed Water Heater Company, 30 Church Street, New York City, N. Y.

PROF. P. DUNNINGTON, Department of Chemistry, University of Virginia, Virginia.

MR. R. KARL HONAMAN, student, Franklin and Marshall College, Lancaster, Pa.

MR. FRANK A. STANLEY, editor and author, 1530 West Main Street, Willimantic, Conn.

### CHANGES OF ADDRESS.

MR. HERBERT S. BERLINER, care of Berliner Gramophone Company, Montreal, Quebec.

MR. FRED. DENIG, 1012 Peoples Avenue, Troy, N. Y.

MR. N. E. FUNK, 5115 Regent Street, Philadelphia, Pa.

MR. CHESTER LICHTENBERG, 140 Glenwood Boulevard, Schenectady, N. Y.

MR. MELVIN L. SEVERY, The Redford, 1334 Commonwealth Avenue, Allston, Mass.

## NECROLOGY.

**Mr. William Stanley,** Great Barrington, Mass.

## LIBRARY NOTES.

### PURCHASES.

ARRHENIUS, SVANTE.—Quantitative Laws in Biological Chemistry. 1915.
BECCARIA, GIAMBATISTA.—Treatise Upon Artificial Electricity. 1776.
CHARNOCK, G. F.—Mechanical Technology. 1915.
COBLENTZ, W. W.—Investigations of Infra-red Spectra, pts. 3 to 7.
EIFFEL, G.—Nouvelles recherches sur la resistance de l' air. 2 volumes. 1914.
GARDNER, W. M., ed.—British Coal-tar Industry. 1915.
GOOCH, FRANK A.—Representative Procedure in Quantitative Chemical Analysis. 1916.
Municipal Year-book of the United Kingdom for 1914.
National Association of Railroad Commissioners, Proceedings, 27. 1915.
Readers' Guide to Periodical Literature, Cumulated, vol. 3. 1910–1914.
Readers' Guide to Periodical Literature, Supplement, No. 3. 1916.
West Virginia, Geological Survey—Lewis and Gilmer Counties. 2 volumes. 1916.
West Virginia, Geological Survey—Wyoming and McDowell Counties. 2 volumes. 1915.
ZENNECK, J., and SEELIG, A. E.—Wireless Telegraphy. 1915.

### GIFTS.

Atlantic Deeper Waterways Association, Proceedings of the Eighth Annual Convention, 1915. Philadelphia, 1916. (From the Association.)
Brandis & Sons Manufacturing Company, Catalogue No. 20 of Instruments of Precision. Brooklyn, N. Y., no date. (From the Company.)
Buffalo Wire Works Company, Catalogue No. 8. Buffalo, N. Y., no date, 1916. (From the Company.)
Concord, New Hampshire, Water Commissioners, Forty-fourth Annual Report, 1915. Concord, 1916. (From the Board.)
Deming Company, Catalogue No. 25 of Deming Pumps for Hand and Power. Salem, Ohio, 1916. (From the Company.)
Denison University, Annual Catalogue, 1915–1916. Granville, Ohio, 1916. (From the University.)
Indian Railway Conference Association, Proceedings of the Locomotive and Carriage Superintendents' Committee, 1915. Moghalpura, Punjab, no date. (From the Association.)
Indiana Engineering Society, Proceedings of the Thirty-fourth and Thirty-fifth Annual Conventions, 1914 and 1915. Indianapolis, 1914 and 1915. (From the Society.)
Iowa State College of Agriculture and Mechanic Arts, General Catalogue, 1916–1917. Ames, Iowa, no date. (From the College.)
Massachusetts Board of Education, Seventy-ninth Annual Report, 1914–1915. Boston, 1916. (From the Board.)
Mysore Government, Meteorological Department, Report on Rainfall Registration in Mysore, 1914. Bangalore, 1916. (From the Department.)

National Commercial Gas Association, Proceedings of the Eleventh Annual Convention, 1915. New York, no date. (From the Association.)

New York Central Railroad Company, Report of the Board of Directors to the Stockholders, 1915. New York, no date. (From the Company.)

New Zealand Official Year-Book, 1915. Wellington, N. Z., 1915. (From the Government Statistician.)

Oberlin College, Annual Catalogue, 1915–1916. Oberlin, Ohio, 1916. (From the College.)

Pennsylvania Board of Public Charities and Committee on Lunacy, Forty-fifth Annual Report, 1914. Harrisburg, 1915. (From the State Librarian.)

Pennsylvania Railroad Company, Sixty-ninth Annual Report, 1915. Philadelphia, 1916. (From the Company.)

Pennsylvania State Librarian, Report, 1915. Harrisburg, 1916. (From the State Librarian.)

Philadelphia Electric Company Section of The National Electric Light Association, Current News, vols. 11 and 12, 1915 and 1916. Philadelphia, 1915. (From the Company.)

Redwood Manufacturers Company, Catalogue No. 7 of Remco Redwood Pipe. San Francisco, no date. (From the Company.)

Royal Canadian Institute, Transactions, November, 1915. Toronto, no date. (From the Institute.)

Society of Naval Architects and Marine Engineers, Transactions, vol. xxiii, 1915. New York City, 1916. (From the Society.)

Sydney University Engineering Society, Journal and Abstract of Proceedings, vols. xviii and xix, 1913–1914. Sydney, no date. (From the Society.)

Taunton, Massachusetts, Water Commissioners, Fortieth Annual Report, 1915. Taunton, 1916. (From the Board.)

University of Colorado, Catalogue, 1915–1916. Boulder, 1916. (From the University.)

University of North Dakota, General Catalogue, 1915–1916. University, no date. (From the University.)

University of the State of New York, Ninety-sixth and Ninety-seventh Annual Reports of the New York State Library, 1913 and 1914. Albany, 1915 and 1916. (From the University.)

University of Vermont, Catalogue, 1915–1916. Burlington, 1916. (From the University.)

Virginia Geological Survey, Bulletin No. X, Surface Water Supply of Virginia, by G. C. Stevens. Charlottesville, 1916. (From the Survey.)

Watuppa Water Board, Forty-second Annual Report, 1915. Fall River, Mass., 1916. (From the Board.)

Wheeler, C. H., Manufacturing Company, Catalogue, Condensing Equipment. Philadelphia, 1916. (From the Company.)

## BOOK NOTICES.

ELEVATORS: A Practical Treatise on the Development and Design of Hand, Belt, Steam, and Hydraulic Elevators, by John H. Jailings. 224 pages, 5½ x 8½ inches, with index; 173 illustrations. Chicago, American Technical Society, 1915. Price, $1.50.

It is common experience that in the development of every sort of mechanical appliance no degree of technical acumen can replace the element of gradual evolution. Consequently the history of such developments in a given field is quite as important in determining a system and design to be adopted as are the fundamental principles employed in the arrangement of and determination of sizes of its component parts. The present volume is devoted to the former phase of the subject and might properly be termed an album of designs representing past and present-day successful practice in elevator driving mechanism. Every variety of platform lift, from the one-story sidewalk lift to the elaborate installations employed in high office building service, is described, along with its various controlling devices. Hydraulic elevators, a type whose value has been proved by widespread adoption for both high and low lifts, is given an adequate share of attention. A concluding chapter describes electrically driven elevators, including those equipped with push-button control for private use, and the recently developed gearless "one-to-one" type which appears to be rapidly superseding the hydraulic systems.

The discussion on the proper proportions of worm gears for the best efficiency, to which several pages are devoted, may be found at length in modern treatises on gearing. The space thus utilized might have been employed to better advantage in giving an outline of the method in current use of determining the proportions of the very long plungers used in high-lift elevators, a problem peculiar to elevator work which will probably not be found analyzed in text-books on applied mechanics. As a descriptive treatise, however, of apparatus of past and present usefulness the book is a welcome addition to the somewhat scant literature of the subject.

L. E. PICOLET.

*The Industrial Arts Index*, which has recently completed its third year, is a cumulative index to 180 engineering and trade publications. It appears in February, April, June, October, and December of each year, and each number is fully cumulated from the beginning of the year to the date of issue.

The December number of each year is the annual volume and indexes all the articles in the publications of the year in one alphabet, under as many subject headings as may be necessary. As a guide to current literature the *Index* is extremely useful.

Requests for sample copies or information as to rates of subscription should be made to the publishers, The H. W. Wilton Company, White Plains, New York.

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## PUBLICATIONS RECEIVED.

*Mechanical Technology*, being a treatise on the materials and preparatory processes of the mechanical industries, by G. F. Charnock. 635 pages, illustrations, plates, 8vo. New York, D. Van Nostrand Company, 1915. Price, $3.

*Practical Physiological Chemistry*, a book designed for use in courses in practical physiological chemistry in schools of medicine and of science, by Philip B. Hawk, M.S., Ph.D. Fifth edition, revised and enlarged. 638 pages, illustrations, plates, 8vo. Philadelphia, P. Blakiston's Son & Co., 1916. Price, $2.50.

*Michigan State Board of Health:* Forty-second annual report of the secretary for the fiscal year ending June 30, 1914. 159 pages, 8vo. Lansing, Mich., State Printers, 1915.

*U. S. Bureau of Mines:* Technical Paper 126, The Casting of Clay Wares, by Taine G. McDougal. 26 pages, illustrations. Washington, Government Printing Office, 1916.

*Oil Fuel*, by Ernest H. Peabody. A paper presented at the International Engineering Congress, San Francisco, Cal., September, 1915, and reprinted from the *Transactions*. 134 pages, illustrations, plates, tables, 8vo.

*Pennsylvania Topographic and Geologic Survey:* Oil and Gas Map of Southwestern Pennsylvania. 30 × 31 inches, with descriptive pamphlet. Harrisburg, State Printer, 1916.

*Athenæum Subject Index to Periodicals, 1915.* Issued at the request of the Council of the Library Association. Science and Technology, with special reference to the war in its technological aspects. 79 pages, quarto. Price, 2s. 6d. Economics and Political Sciences: Law. 28 pages, quarto. Price, 1s. London, The Athenæum, 1916.

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**Air-friction Automobile Speedometer.** ANON. (*Scientific American*, vol. cxiv, No. 16, April 15, 1916.)—Depending upon the principle of air friction and consisting essentially of two metal cups fitting one into the other, but not touching at any point, a speedometer has been developed to a commercial stage after three years' experimenting on the part of a leading watch company. The new speedometer is unique in that it does not employ the centrifugal or magnetic principle as do other types of speedometer in general use; instead, it relies on the friction of air as developed by the metal surfaces. The two main components of the speedometer in question are a driving cup, which is rotated by power from one of the automobile wheels through flexible shafting, and, suspended over and around it, a driven cup The driven cup, carrying on its periphery indicating the miles per hour attained, is inverted over and around the driving cup. This cup, as is also true of the driving cup, in reality consists of a double cup. In operation, the driven cup generates air friction which, were it not for a regulating hairspring serving normally to maintain the indicating cup at the zero marking, would cause the latter to revolve. The hairspring is so adjusted that the speed readings are proportional to the angular deflections, experiments having shown that the air friction varies directly with the speed.

# CURRENT TOPICS.

**Coating Metals with Zinc.** ANON. (*Iron Trade Review*, vol. lviii, No. 15, April 13, 1916.)—An interesting instance of adopting a process to changed conditions is found in a new apparatus for coating metals with zinc film. The Metals Coating Company of America has developed the Schoop metal spraying process in which zinc wire or other metal wire is melted in a gas flame and projected under pressure onto the surface to be coated. Under present conditions in the metal market this wire has become exceedingly expensive. To fill the need for a less costly process, the apparatus has been modified to permit the employment of zinc in the less costly form of dust. It consists of a conical receptacle which has another similarly-shaped receptacle inside, with a small space between. Zinc dust is placed in the inner cone and compressed air is admitted through a hose at the top of the space between the two cones. A valve at the bottom of the inner compartment allows the zinc dust to be caught up by the air current and carried through a discharge tube to a spraying device. The zinc dust is there blown from an inner nozzle through an acetylene gas flame, the heat of which is sufficient to melt the zinc. In the melted condition the particles of zinc are projected at high velocity upon the surface to be coated by the action of the blast. Adjustable valves regulate the quantity of zinc dust allowed to pass into the air current and also the quantity of gas used to melt the metal.

The apparatus weighs about twenty pounds and uses air at a pressure of about five pounds per square inch. Acetylene gas, the heating agent, is easily available, and has been found to give good results with zinc dust. The present cost of zinc wire is about $1.25 per pound, while zinc dust, which is a by-product of the zinc smelter, may be obtained at about thirty cents per pound. The portability of the apparatus adds to its usefulness for work in the field in coating structural or bridge steel with a film of zinc to resist corrosion. Even at ordinary price levels the use of zinc dust is less expensive than wire, a feature which considerably broadens the application of this method of coating and makes possible its use on much larger surfaces than when zinc wire is used.

**Light Transmission Through Telescopes.** M. KOLLMORGEN. (*Transactions of the Illuminating Engineering Society*, vol. xi, No. 2, March 20, 1916.)—As is generally known, the amount of light energy which falls upon a glass surface is divided into two parts: a smaller one which is reflected back into the original medium, and a larger one which continues into the glass and is refracted in it and, in the telescope, forms an image. The relative amounts of these two quantities

for vertical incidence can be readily computed in terms of the refracted indices of the media beyond and before the surface of incidence. The amount of light transmitted through each element of an optical instrument may be between 85 and 95 per cent. of the available total. Hence the efficiency in an optical instrument having a considerable number of elements, measured by the continued product of the efficiency of each component, may be objectionally low. For example, in a modern periscope gun-sight the efficiency of light transmission is 36.2 per cent., and this figure is reduced to 32.5 per cent. by absorption of the combined thickness of prisms and lenses. In some modern periscopes for submarines barely 20 per cent. of the available light reaches the observer.

It would thus be a desirable thing if it were possible to treat the glass surfaces in such a way as to reduce reflection. It has been known for some time that it is possible to increase the reflecting power of a surface. Professor Wood, of Johns Hopkins University, some years ago made the remarkable discovery that by coating a glass surface with a thin solution of collodion a degree of reflection could be obtained quite out of proportion to the refractive indices of either the glass or the collodion itself. For optical work, however, just the opposite is desired, and, as very often is the case, chance has given us a hint which has already produced very desirable results. In 1904, H. Dennis Taylor, the well-known English lens expert and designer of the Cook lens, saw a very badly-oxidized photographic lens which had been returned to be repolished . Possibly just to find how much light was lost through this oxidation, he exposed two plates under identical conditions, one through a perfectly new, untarnished lens, the other the badly-oxidized specimen. To his great surprise he found that the plate taken with the badly-tarnished lens had received considerably more light than that taken with the new lens, and, acting upon this hint he sought means of oxidizing lenses artificially. He soon found chemicals that would attack at least some of the glasses used in optical instruments. His treatment consists in immersing the lens immediately after polishing for a short time in an aqueous solution of ammonia and hydrogen sulphide. Experimenting further along the same lines, the writer has found means of oxidizing most of the glasses used in optical work. Using a barium crown glass of refractive index of about 1.6, the untreated glass, in agreement with the Fresnal formula and with photometric measurement, transmitted 89 per cent. of the light, while of a set of similar treated samples the best transmitted 96 per cent. When a number of these are mounted in series, the difference in reflecting power is easily observed by the unaided eye, but the photometer shows that the amount of light taken away from the reflected part is actually not absorbed by the roughness of the surface, but is added to the transmitted part.

**Oxy-acetylene Welding in Heavy Sections.** C. K. BRYCE. (*Steel-Iron*, April, 1916.)—Fusion welding by the oxy-acetylene process in both cast iron and steel of heavy sections is meeting with greater favor as the engineering and mechanical fields gain more confidence in the process and grow to appreciate its merits and limitations. The process has been established for a sufficient length of time to point out the fundamental methods of procedure. As the subject is more carefully studied, various experiments and changes will be introduced which will add greatly to the quality and economy of the process. In the present stage of the process experience has shown certain limitations.

In steel welding, where the section welded is submitted to strain, the greatest success has been attained in sections under six inches if square and five inches if round. In plate work, metal 1¼ to 1½ inches in thickness has been welded satisfactorily. In cast iron the size of the section is limited only by the amount of pre-heating that can be given it and effect the resulting expansion. Sections as heavy as 12, 14, and 16 inches have been welded successfully. All heavy work should be pre-heated. In cast iron this is necessary in order to eliminate chance of failure through contraction and expansion strains. While the chance of failure in steel is not as great because of this, nevertheless the internal strains in the weld will be reduced by the procedure. In additon to offsetting the mechanical difficulties, pre-heating should be used to introduce a certain quantity of heat into the metal that would otherwise be supplied by the blow-pipe, thus considerably reducing the cost of the operation.

**Beams Without Lateral Support.** R. FLEMING. (*Engineering News*, vol. 75, No. 14, April 6, 1916.)—The percentage most widely adopted of tabular safe loads for beams supported sidewise to be used for beams not so supported are those given in the Pencoyd book, "Steel in Construction," 1884, edited by James Christie. As long as it was published the Pencoyd book retained the table of these values. The table will be found in editions of the Carnegie "Pocket Companion" for 20 years previous to 1913. It is still in the handbooks of the Bethlehem Steel Company, The Jones & Loughlin Steel Company, and the Phœnix Iron Company. It is also in Kent and Kidder and quoted by many writers. To many who have accepted these values as the result of precise investigation, Mr. Christie's views on the subject 25 years after they were first published will be a surprise.

"Some experiments were made on beams of considerable length in proportion to cross-section and without lateral support, the object being to ascertain approximately how the working loads should decrease as the length of the beam increased. As I remember it, the results of these experiments were unsatisfactory, and, although tables were formulated suggesting a scale of reduction for loads on

long beams without lateral support, yet these tables had neither a rational nor an experimental basis, but were derived by a general estimate of probabilities. For long beams, when the beam is reasonably straight and its load free from vibration, a large load appeared to be safely borne. But this was not the case when lateral vibrations were set up. The long beam heavily loaded appeared to be in a state of unstable equilibrium."

Subsequent investigation does not appear to have placed these load-reduction factors on a more rational basis. The writer suggests the formula $19000-250\ l/b$ ($l$ = unsupported length; $b$ = width of compression flange) for the unit stress, to be used when the lateral unsupported length exceeds 12 times the width of the compression flange. The length should in no case exceed 50 times the width of the compression flange.

**Bahia's Trade in Diamonds and Carbonados.** R. FRAZER, JR. (*U. S. Commerce Report*, No. 41, February 18, 1916.)—There is a considerable business done at Bahia (Brazil) in both rough diamonds and carbonados (miner's diamonds), but exact figures cannot be given as to the volume of the trade. That it is of some importance, however, is evident from the fact that 11,803 carats of rough diamonds and 3714 carats of carbonados were invoiced at the Bahia consulate for shipment to the United States alone in 1915. It is interesting to note that the state of Bahia is the only part of the world in which high-grade carbonados are found. The mining of precious and semi-precious stones is carried on here chiefly by individuals, or at least by small-scale enterprises, and not by large companies that both mine and export their own product. The stones, therefore, arrive at Bahia, the centre of the trade, singly or in small lots, and are there bought up by middlemen and exporters.

The stones most difficult to obtain in any quantity are, of course, those larger than ¾ to 1 carat, but stones of the former weight and mêlès of ½ carat or less are comparatively plentiful. Various lots of rough diamonds and carbonados of mixed sizes have lately been invoiced at this consulate at prices ranging from $9 to $30 and $15 to $36 per carat respectively, while the average prices for the year 1915, as declared at this consulate, were $18 per carat for diamonds and $32 for carbonados. The average value of the diamonds exported was, therefore, less per carat than the carbonados. At present, mêlès of ½-carat stones or smaller should be obtainable at about $10 per carat; ¼-carat stones, $12 to $14; ½-carat, $16 to $20; ¾-carat, $20 to $23; 1-carat, $25, and from 2 carats upward, $35. It is believed that these prices may be taken as approximately average ones, although it is impossible to give exact figures with respect to articles which vary so greatly in value with small differences in quality.

Bort is not plentiful at Bahia, and very little is dealt in, it being said that the prices asked for it are higher than for bort from other origins.

**A Method for the Determination of Free Caustic Alkali in Soap.** F. H. NEWINGTON. (*Journal of the Society of Chemical Industry*, vol. xxxv, No. 2, January 31, 1916.)—It is well known that the addition of common salt to an aqueous solution of soap "salts out" or completely separates the soap. This separation of soap can be effected equally well by means of sodium sulphate, and any free caustic alkali in the sample is separated by the aqueous sodium sulphate solution. The caustic alkali thus extracted is free from soap, and may be readily determined by titrating with N/10 sulphuric acid, using silver nitrate as a spot indicator. The advantage of using sodium sulphate to "salt out" the soap is that by this means a solution is obtained which will not produce an insoluble compound with the silver nitrate used as an indicator in the titration. If sodium chloride were used to salt out the soap, the solution obtained would, of course, form the insoluble chloride with the silver nitrate and hence leave no soluble silver salt to react with the hydroxide. A 5 per cent. solution of silver nitrate is sufficiently strong to precipitate any small amount of chloride that may be dissolved from the soap, and still to leave an excess of silver nitrate to react with the hydroxide. This method has been found quite satisfactory in testing toilet, household, and soft soaps, as well as soft soap substitutes.

**Radium, Uranium, and Vanadium in 1915.** ANON. (*U. S. Geological Survey Press Bulletin*, No. 256, January, 1916.)—Radium, uranium, and vanadium are closely connected in occurrence in the principal fields, Colorado and Utah, but in 1915, although the European war caused a great slump in the production of ores of radium and uranium, it caused a considerable increase in the production of ores of vanadium.

According to reports for 1915 received by the United States Geological Survey and compiled by Frank L. Hess, the output was 23.4 tons of uranium oxide and 6 grammes of radium contained in the carnotite ores produced, and 635 tons of vanadium contained in the carnotite ores shipped and in the chemical concentrates from the roscoelite ores. In 1914 the ores produced contained 87.2 tons uranium oxide, 22.3 grammes radium, and 435 tons vanadium.

The United States has much the largest known radium-bearing deposits of the world, but the market for radium is mostly in Europe, for, though Americans like to feel that they are sufficiently progressive to take hold of and use to the full new discoveries, inventions, and processes, yet the European municipalities and hospitals have been buying and utilizing most of the radium produced. When the war began, therefore, causing European money to flow into other channels, the demand for radium fell off so greatly that there was practically no market for radium or uranium ores in the early part of 1915, and very little market during any part of the year. Mining of carnotite ores, except by the National Radium Institute (Inc.) under the

supervision of, and in coöperation with, the Bureau of Mines, and except for such work as was necessary for assessment work to hold claims, was nearly stopped.

The Institute mined nearly the 1000 tons of ore contracted for from the Crucible Steel Mining and Milling Company's claims in Long Park, Montrose County, Colo., and obtained 70 tons of concentrates, carrying about 3 per cent. of uranium oxide, by concentrating material carrying 0.7 per cent., which had been thrown on the dumps. The Institute fully accomplished its purpose to work out a practical process of producing radium at a cost much below the market price of the element and crystallized out radium salts containing 6 grammes of the element. It delivered during the year 3.006 grammes of radium (element) at a cost of $37,599 per gramme. Near the close of the year 1.1 grammes of radium (element) was contracted for by a private company for $132,000, or $120,000 a gramme. This comparison shows the great success of the work of the Bureau of Mines. Its ore concentration method seems to have also been highly successful. After mining its quota of ore from the Crucible Steel Mining and Milling Company's property, the Institute came into the market as a purchaser of ore.

In the later half of the year Dr. W. A. Schlesinger and associates established a radium reduction plant in Denver. They acquired an interest in the Copper Prince claims, from which ore was mined, and bought a further quantity. Ore carrying about 5000 pounds of uranium oxide, containing about 640 milligrammes of radium, was treated during the year.

The Carnotite Reduction Company, made up of Dr. H. N. McCoy, of the University of Chicago, and associates, purchased from Galloway and Belisle a quantity of ore which had been stored in Placerville, Colo., and the radium will be extracted in Chicago. The company will mine ore from claims it has bought.

The Standard Chemical Company did no work on its claims except that required by law, but in this work produced and shipped a quantity of ore from its properties in Colorado and Utah, and purchased, it is stated, a considerable number of claims. It was reported in December that the company had produced a total of 14 grammes of radium (elemental) and that its ore had averaged 1.7 per cent. uranium oxide. Probably between 4 and 5 grammes of this quantity was produced during 1915.

The production of radium salts in this country during the year was probably nearly 11 grammes.

Only a small quantity of ore is thought to have been shipped to Europe during the year. J. S. McArthur & Co. shipped one lot of ore from its claims near Greenriver, Utah, to Glasgow, Scotland.

**Peptone as an Addition Agent in Stannous Ammonium Oxalate Baths.** F. C. MATHERS and B. W. COCKRUM. (*Proceedings of the American Electrochemical Society*, April 27–29, 1916.)—

Tests of tin-plating baths by these investigators indicated that the best tin deposit is obtained from a sannous ammonium oxalate bath containing peptone as an addition agent. Without the peptone the deposit is of no value as a protecting coat, because it consists of projecting needle-like crystals. The effect of the peptone is very remarkable. As soon as it was added, the tendency to form the projecting, loosely-adhering crystals ceased and the deposits became so smooth and finely crystalline that thick cathodes (0.5 to 1 cm. thick) could be prepared, and so firm and coherent that shavings could be cut from the deposit with a knife. Clove oil, glue, gelatine, and formin, agents which have been found effective with other metals, were practically without any beneficial influence in preventing the formation of crystals. Carbon disulphide, even in small amounts, made the deposit spongy and non-adherent, a condition which persisted until the carbon disulphide was exhausted, when the deposit again became crystalline.

The addition of peptone to the stannous ammonium oxalate bath is essential for the production of a thick, smooth, finely crystalline deposit of tin. No other tin bath (except possibly the sulphide, which was not tried) is known from which such a thick, smooth deposit can be obtained. A good composition of bath is : 5 per cent. stannous oxalate, 6 per cent. ammonium oxalate, 1.5 per cent. oxalic acid, and 0.25 per cent. peptone. The stannous oxalate may be easily made by precipitating a solution of stannous chloride with oxalic acid. The bath was run at room temperature at 0.4 ampère per square decimetre (3.6 per square foot). The solution must be stirred at intervals.

**Wireless Achievements at Tufts College.** ANON. (*The Electrical Review and Western Electrician*, vol. 68, No. 16, April 15, 1916.)—The transmission of music by wireless with a small amount of power, giving a range of more than 100 miles, so that ships at sea have picked up tunes, has been brought about at the station of the American Radio & Research Corporation at Tufts College, Massachusetts, of which Harold J. Power is general manager. The mere fact of sending music to the distance mentioned is not of itself a remarkable feat, but by means of a novel method of introducing the sounds in the radiated waves, resulting in articulation and loudness in the waves received, a marked gain has been achieved.

To provide the high-frequency current necessary, Professor Power employed an oscillon bulb, the invention of Lee de Forest, of New York. It is recognized that there are two important factors in the successful transmission of wireless telephone messages. One is the generating of high-frequency currents, and the other is the modulation in accordance with the voice or the music to be transmitted. It is the latter of these two problems that Professor Power is especially interested in, because the De Forest oscillon is recognized as a perfect means of generating the needed high-frequency current. It has been possible for some time to obtain sufficient power to

transmit telephone messages to any distance, but how to introduce the voice in high-power stations in a practical manner is the great problem of radio telephony, and to this branch of work Professor Power is now devoting much attention. His device for introducing the voice is far from perfected as yet, but, from reports thus far received, successful results have been obtained. Operators at several stations on Cape Cod have reported recording the strain of well-known popular airs produced by a phonograph, and, in some instances, steamers entering Boston reported picking up the music more than 100 miles out from port.

The radio station is one of the most complete in the country. Students at Tufts College have the facilities at their disposal for experimental work, though the plant is owned by a private corporation, and a number of valuable results have been developed by numbers of the Tufts Wireless Club.

**Land Drainage by Means of Pumps.** S. M. WOODWARD. (United States Department of Agriculture, Bulletin No. 304, November 19, 1915.)—The drainage of low-lying lands by the use of pumping machinery to lift the drainage water over levees into adjacent streams or other drainage channels is a recent development in this country. Along the banks of our larger interior rivers considerable areas of bottom land are subject to overflow from the adjacent streams during the high water occurring usually with great regularity throughout the spring and early summer months. Such lands in their native state do not become dry enough to be subjected to ordinary cultural operations until well toward the middle of the summer, and hence can not be used for growing ordinary crops. In this natural condition they are therefore good for nothing but pasture, and have accordingly but little agricultural value.

So long as there exists in a locality any unoccupied or unutilized higher land suitable for agriculture there is little demand for the use of lands lying so low as to require the use of pumps. But the present high price of agricultural land justifies a heavy expenditure for the conversion to a productive state of areas formerly considered almost valueless, especially in those regions where agricultural land values are particularly high, either on account of unusually favorable natural conditions or the proximity of large centres of population.

Drainage by means of pumps has been carried on in European countries for the last 100 years, and has been rapidly increasing in this country during the last 25 years. Through this extensive experience, including numerous failures, a considerable amount of knowledge is now available on the subject of the proper arrangement and the requisite capacity of pumping plants. Notable examples of successful work of this character are found in Holland, eastern England, and in Ireland, while large marsh areas in both northern and southern Italy depend upon pumps for adequate drainage. The pumps which were first used were the well-known scoop wheel and

Archimedean screws which were driven by windmills. In modern installations, however, the pumps are invariably of the centrifugal type, driven by a steam, gas, or electric motor.

**Performance of 30,000-Kw. Steam Turbo-generators.** ANON. (*Electrical World*, vol. 67, No. 20, May 13, 1916.)—The extent to which the steam turbine has displaced the piston engine in large units is strikingly shown by the performance of the 30,000-Kw. units recently installed in the Seventy-second Street Station of the Interborough Rapid Transit Company of New York. In 1900 this station housed eight Reynolds Allis-Chalmers steam engines of a double combination horizontal-vertical cross-compound design. Each unit was rated at 5000 Kw., with a maximum rating of 7500 Kw. In a space no greater than taken by one of these units a 30,000-Kw. turbine unit now stands, operated from the same boilers now equipped with underfeed stokers, and superheaters to give 200 degrees of superheat when the boilers are delivering three times their rated output. The boiler pressure is 205 pounds per square inch gauge. The steam engines operated originally at 175 pounds gauge and no superheat. The cost of the engines, generators, and condensers was $40 per kilowatt, while the cost of the new turbine and condensers is $9 per kilowatt. The steam engine water rate was 17 pounds per kilowatt-hour, as compared with about 11.4 for the turbines operating under similar load conditions.

The performance of the unit in outclassing in operating efficiency, cost, space requirements, and ability to handle swinging loads amply establishes the enviable position of the steam turbine as a prime mover. The old engines, which at the time of their installation represented the last word in engine design, found no purchaser but the junk dealer. It is also interesting to note that, although it was decided two years ago to use this new type of turbine, changes in the art and operation in the interim have been such that the company will now install a 70,000-Kw. cross-compound unit with three generators, any one of which may be operated independently if desired. Thus this art of generating electricity in steam-turbine driven stations has advanced to a point where, up to load factors of approximately 60 per cent., a kilowatt-hour of electrical energy can be manufactured more cheaply by this means than by water power.

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